BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

OF THE USSR

Division of Chemical Science

(IZVESTIIA AKADEMII NAUK SSSR)

(Otdelenie Khimicheskikh Nauk)

IN ENGLISH TRANSLATION

DENDRITIC CRYSTALLIZATION

by D. D. SARATOVKIN

2nd Edition,
Revised and Enlarged

Translated from Russian

THIS SIGNIFICANT volume has been extensively revised by the author from the 1953 edition; in particular with *fresh material derived from observations under the stereoscopic microscope.*

The first section deals briefly with some general concepts on crystallization, drawing an important distinction between *genetic* and *structural* types of crystals, including some aspects of the *defect crystal state.* The second section covers at length the illuminating ideas and observations of the 19th-century Russian metallurgist D. K. Chernov, who proposed many of the basic ideas of dendritic crystallization. The third section is an extended survey of current views on dendritic crystallization, in which the ideas of many Soviet and other scientists are briefly summarized and criticized. Section four presents the growth forms of real crystals; all types are reviewed, but only dendritic or closely related forms are selected for subsequent investigation.

Following sections discuss the causes and forms of crystal growth, with *detailed applications* to certain substances that have been extensively studied *(particularly the ammonium halides),* and to eutectics in metal and organic systems; an extensively revised presentation on steel castings which provides a lucid explanation of how the various structures found in real castings can be fitted into the author's theory of dendritic crystallization. Nearly all the concepts developed earlier in the book are utilized in this final section.

The main bulk of the volume contains many *original* and *unpublished* ideas and observations, and is an excellent example of the modern macroscopic approach to the crystalline state by an experienced worker concerned with the infinite variety of real crystals—all of which is enhanced by a *profusion of explanatory line diagrams and sets of stereoscopic photographs.*

CB translations are by bilingual scientists, and include all photographic, diagrammatic and tabular material integral with the text.

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Cloth-bound; 126 pp., illustrated; $6.00

CONSULTANTS BUREAU, INC.

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AVOGADRO'S LAW AND SOME MODERN FORMULATIONS OF IT*

A. F. Kapustinskii

One hundred years have passed since the death of the Italian scientist Lorenzo Romano Amedeo Carlo Avogadro de Quaregna e di Cieretto (1856-1956) [1]. Modern atomic and molecular theory is based on the hypothesis advanced by Avogadro in 1811, namely that equal volumes of gases contain equal numbers of molecules when they are at the same temperature and pressure [2]. The general acceptance of the hypothesis was far from immediate; it occurred, in fact, only after the death of its author: its final acknowledgement came after the Carlsruhe Congress of 1860, at which Cannizzaro gave a convincing demonstration of its preeminence over other views. Soon afterwards the hypothesis was deduced by Clausius and Maxwell from the kinetic theory of ideal gases, the starting point being the equipartition of energy among the degrees of freedom. Mendeleev not only appreciated the great importance of this hypothesis to science, but actively worked for its firm establishment in chemistry[3]: he derived the formula $M = 2D$, which, as Faershtein [4] pointed out, may rightly be called the Avogadro-Mendeleev equation. At the start of this century the hypothesis was already beginning to be regarded as a law, and Nemst [5], for example, considered that this law, along with thermodynamics, lies at the basis of theoretical chemistry. In the course of time, Avogadro's law not only received decisive experimental confirmation, but was extended to some new fields of science. The most natural extension of the law was to states showing a certain analogy to gases.

As is well known, the basic idea of van't Hoff's physical theory of solutions is the concept of the similarity between the dissolved and gaseous states of matter. This enabled the author of this theory to establish that at equal temperatures and osmotic pressures equal volumes of solutions contain equal numbers of dissolved molecules — a statement which may rightly be called the law of Avogadro and van't Hoff.

The attention of van't Hoff was concentrated on solutions of nonelectrolytes. Studying electrolytes, Arrhenius arrived at the concept of dissociation into ions, which gradually developed into the theory of strong electrolytes, regarded as completely dissociated systems. It is obvious that, as such systems do not contain undissociated solute molecules, still another formulation, also referring to solutions and also associated with the concept of osmotic pressure, is possible: at equal temperatures and osmotic pressures equal volumes of solutions of strong electrolytes contain equal numbers of ions. As ions are qualitatively different from molecules as forms of matter, and as solutions of electrolytes are of great importance in chemistry, this further formulation also has a right to exist: it may be called the Avogadro-Arrhenius law.

Although the limited character of the above generalizations is clear and although it has long been known that both for gases and for solutions the simple laws are strictly valid only at high dilution, i.e. at low pressures of gases and at solution activities of close to unity, this matter was not adequately clarified before the classical investigations of Daniel Berthelot [6], which permitted a precise formulation of the law that has become one of the most rigorous and irreproachable laws of physical chemistry, now called [7] the Avogadro-Berthelot law: equal volumes of gases at equal temperatures and equal infinitesimally low pressures contain equal numbers of molecules. It is obvious that a similar correction relating to infinitesimally low osmotic pressure must be introduced into the formulation referring to solutions.

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* Paper read at the first session of the Colloquium on Physicochemical Analysis of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, Moscow, December 13, 1956.

TABLE 1

Relation of the Mean Density of the Electron Gas in an Ion to the Charge of the Ion

Ion	Number of electrons $\underline{m}$	Volume V (A^3)	Mean density of electron gas $\underline{d}$	Ion	Number of electrons $\underline{m}$	Volume V (A^3)	Mean density of electron gas $\underline{d}$
At "pressure" of 1 (i.e. ionic charge $\eta = 1$)				At "pressure" of 3 (i.e. ionic charge $\eta = 3$)			
Na	10	3.94	2.6	Al	10	(0.78)	(12.5)
K	18	9.86	1.8	Sc	18	2.40	7.5
Rb	36	13.85	2.6	Yt	36	4.99	7.2
Cs	54	18.82	2.9	La	54	7.61	7.1
Average value of density			2.5	Average value of density			7.3
At "pressure" of 2 (i.e. ionic charge $\eta = 2$)				At "pressure" of 4 (i.e. ionic charge $\eta = 4$)			
Mg	10	1.94	5.3	Si	10	(0.25)	(33.3)
Ca	18	4.99	3.6	Ti	18	1.10	16.3
Sr	36	8.58	4.2	Zr	36	2.76	12.8
Ba	54	12.25	4.4	Ce	54	4.45	12.3
Average value of density			4.4	Average value of density			13.8

Note: Aluminum and silicon ions show great discrepancies; the data referring to these ions are placed in parentheses and are not taken into account in the calculation of the averages.

The use of the concept of limiting states and of the method of limiting densities made it possible to determine the molecular weights of gaseous substances with almost unprecedented precision. The volume of one mole under standard conditions and Avogadro's number now belong to the so-called fundamental physical constants. A good example of the accuracy now attained in the determination of these quantities is afforded by the recently published work of du Mond and Cohen [8], who applied the method of least squares to the analysis of the most accurate estimations of Avogadro's number made by sixteen [1] different experimental methods; they arrived at the value:

$$N = 6.02472 \, (\pm \, 0.00036) \cdot 10^{23}$$

As Avogadro's law is one of the ideal gas laws, it should be applicable to systems of particles that are independent of one another, i.e. have extremely small interactions. Gases at low pressures correspond closely to this model. It might be thought that its extension to solutions is much less rigorous and must be associated with appreciable discrepancies due to the presence of appreciable interaction forces, both between the dissolved particles and between these and the solvent particles. Nervertheless, though the accuracy is somewhat lower, the generalization holds satisfactorily in this case also.

Until now we have considered volumes containing atoms, ions, and molecules. It would be interesting for us to proceed to a consideration of the spaces occupied by the ions and molecules themselves. In ions the role of pressure is played by charge, which draws the electrons together into the given spherical volume, i.e. the positive charge of the ion, which can be regarded as a point charge at the center of the ion. With respect to this center the electrons are localized at various energy levels described by quantum chemistry. However, it is permissible to speak of a certain averaged picture and to consider the mean density of the electron cloud in the ion, understood as the ratio of the total number of electrons to the total volume of the ion. It will be obvious that we cannot here attain the accuracy characteristic of gas systems, because the interactions of the particles are here considerably stronger than in the case of gases. It is not difficult to show, however, that the law of the eminent Italian scientist is again manifested here, at least if we consider those ions which, on analogy to the ideal gases, we may term ideal ions, i.e. the eight-electron ions (preferably cations) of the inert-gas type, the structures of which are closest to the ideal spherically symmetrical structure.

TABLE 2

Verification of the Proportionality between the Density of the
Electron Gas and the Ionic Charge ($d = 2.4 \cdot \eta$)

Ionic charge η		1	2	3	4
Mean density of the electron gas $\underline{d}$	Found (Table 1)	2.5	4.4	7.3	13.8
	Calculated from the equation $d = 2.4 \cdot \eta$	2.4	4.8	7.2	9.6

TABLE 3

Verification of Avogadro's Law for the case of Equally Charged
Anions

Ion	F^-	OH^-	Cl^-	HS^-	Br^-	HSe^-	I^-	HTe^-
Number of electrons in ion	10		18		36		54	
Volume of ion (A^3)	10	12	25	28	32	34	45	45

As we showed previously [9], for such ions the effective radius r can be expressed to a close approximation in terms of the total number of electrons m and the valence or charge of the ion η by an equation which contains no empirically chosen proportionality coefficients:

$$ r = \frac{\lg m}{\eta^{1/2}}. \tag{1} $$

If we therefore regard the electrons as moving, more or less uniformly as in a gas, in a volume equal to the effective spherical volume of the ion, the size of which depends on the forces attracting the electrons to the point nucleus (these forces, calculated per unit surface, can be likened to pressure), it is not difficult to deduce the equation of state:

$$ \eta \cdot V = \text{const}, \tag{2} $$

which, as we have shown previously, receives almost as much support from experiment as the corresponding Boyle-Mariotte law for gases [9]. The volume entering into this equation is obtained by the usual formula:

$$ V = \frac{4}{3} \pi r^3 $$

after substitution for the radius from Equation (1):

$$ V = \frac{4}{3} \pi \cdot \frac{(\lg m)^3}{\eta}. \tag{3} $$

As equations of the Boyle-Mariotte type are found to be satisfactorily applicable not only to gases and solutions, but also to an electron gas in the volume of an ion, it is natural to apply also the more general Mendeleev-Clapeyron equation of state:

$$pV = nRT, \tag{4}$$

which, applied to the density (d = n/V) of a gas at constant temperature, indicates proportionality between pressure and density:

$$p = dRT$$

or

$$d = Ap,$$

in which 1/RT = A, a constant. In a similar way the following equation should hold for an electron gas:

$$d = A\eta. \tag{5}$$

It follows from Equation (5) that for all ions of a given charge the mean electron density d, i.e. the number of electrons in a cubic Angstrom unit, should be the same. This is readily verified (Table 1), because the required data are well known for all eight-electron ions of various charges.

Table 1 shows that the constancy of the mean electron density of all ions of given charge is indeed confirmed by experiment. In spite of the fact that both the numbers of electrons and the volumes of the ions vary within wide limits (an almost sixfold variation), the mean density of the electron gas remains unchanged* .

Also, the average values found for the density of the electron gas for each value of the charge is proportional to the "pressure", i.e. to the charge of the ion, as indicated by Equation (5). The empirical proportionality coefficient A is 2.5 (Table 2).

This proportionality holds only approximately, however; as will be seen from Table 2 and as is required by theory, for the highest of the densities considered (a charge of 4) there is a considerable discrepancy. The higher the charge of the ion, in fact, the greater the "compression" experienced by the electron gas, and the greater will be the departures from the simple ideal laws for the state of such a system. The analyses of these departures are of interest on their own account: they should increase with increase of ionic charge at a much higher rate than that at which the departures from the ideal laws increase with pressure in the case of gases, for they are approximately proportional to the product of the charges (+ and −), i.e. proportional to the square of the valence. In order to leave these approximate estimates and make a closer approach to the real picture, we shall draw a smooth curve through all the points representing the average densities of the electron gas (Table 1) in a graph showing their relation to the ionic charge (see figure). We obtain a steeply rising curve tending to infinity already at values of η approaching six. In this lies one of the explanations of the well-known fact of crystal chemistry, namely that ions of valence six and higher are never found in crystal lattices. Ions of valence greater than five cannot be realized in crystals because their presence would require an infinitely high density of electron gas in the ion, which is impossible.

The simple gas laws are therefore applicable both to solutions and to electrons within the volume of an ion but whereas in the first case in place of the usual pressure we have the osmotic pressure, in the second case the same part is played by the ionic charge. Now, after the above detailed examination of this question, we may make the following step and pass directly to Avogadro's law. For this purpose we may make use of a method of derivation that is reminiscent in all its main features of the derivation of Avogadro's law from the kinetic theory

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* This approach provides a simpler approximation to the problem of the equation of state of an electron gas than that provided by Fermi-Dirac statistics [10]. To a certain extent the former treatment supplements the latter by the concept of the ideal ionic state, while retaining calculations of the degenerate state as before. We therefore do not discuss the concept of "temperature", but in comparing ions we refer only to the identity of conditions. It is interesting that the statistics, unlike the theory of gases, yield an analog of the Boyle-Mariotte law which remains the same irrespective of temperature, so that the equation of state for an electron gas is a relation between pressure and volume only, as in our treatment in this paper.

of gases, but is not at all identical with it, as will be seen from the footnote on page 644.

Let us consider two ions of equal volume and existing under identical conditions.

We shall write equality of "pressures" (charges) as

$$\eta_1 = \eta_2 \tag{6}$$

and equality of volumes $V_1 = V_2$ (cf. (3)), as

$$\frac{4}{3}\pi\frac{(\lg m_1)^3}{\eta_1} = \frac{4}{3}\pi\frac{(\lg m_2)^3}{\eta_2}. \tag{7}$$

The two equations (6) and (7) are satisfied simultaneously only when

$$m_1 = m_2, \tag{8}$$

which is what was required to be proved. Hence, under identical conditions two ions of equal volumes contain equal numbers of electrons. This is Avogadro's law extended to atomic electronics.

As it is difficult in practice to find ions of equal volumes and equal charges, for the correctness of Avogadro's law in this new field, it is simpler to find a proof which is borrowed from the crystal chemistry of anions [11].
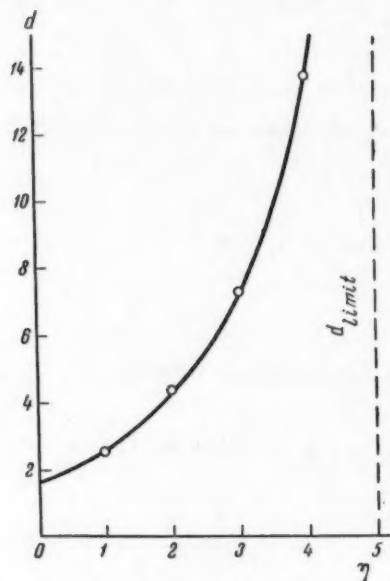
Relation of the mean value of the density of the electron gas in the volume of an ion $\underline{d}$ to the ionic charge η; d_{limit} is the limiting infinitely high density of electron cloud corresponding to and ion having five units of charge in the lattice of a solid.

Hydride ions of elements of Group VI of Mendeleev's system are formed by the deep penetration of the proton into the electron envelope:

$$\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:\right]^{=} + \overset{+}{\overset{\cdot\cdot}{H}} \rightarrow \left[:\overset{\cdot\cdot}{X}\overset{\cdot\cdot}{\underset{\cdot\cdot}{H}}:\right]^{-},$$
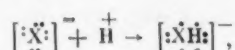
confirmation of which is provided by their very low dipole moments (about $0.5 \cdot 10^{-18}$). In the calculation of their volumes from their radii the supplementary effective volume due to the presence of the proton must be taken into consideration, and this may be done very tentatively by the introduction in all cases of a correction of 0.1 A in the radii. These ions are spherical and have an eight-electron outer shell. As will be seen from Table 3, the equality in the volumes of the ions containing equal numbers of electrons is confirmed: isoelectronic halide ions and hydride anions of Group VI have almost equal volumes and, as would be expected, this rule is observed more closely as the number of electrons in the ion increases. Unfortunately, we are compelled to confine ourselves to these examples because crystal chemistry offers very few possibilities for such comparisons.

The observed departures from mean values are quite natural for such complex systems. It must not be forgotten that, as shown already by Berthelot [12], even in the case of real gases molar volumes differ from one another by 1-2% (e.g. H_2 22.4, HCl 22.2, SO_2 21.9 liters).

Hence, when it is taken into account that all the above applies only to ions of ideal structure, we see that experiment yields satisfactory confirmation of the theoretical deduction from Avogadro's law in the field of atomic structure, i.e. the equality of the volumes of isoelectric ions under identical conditions. This can be added to the already existing formulations that extend the field of application of Avogadro's law.

SUMMARY

1. In the century that has elapsed since the death of the great Italian scientist Avogadro (1856-1956), the hypothesis that he advanced in 1811 concerning the equality of the numbers of molecules in equal volumes of gases under identical external conditions has become the basis of modern atomic and molecular theory; it can be regarded not as a hypothesis, but as a law of nature.

2. The field of application of this important generalization has been found to be considerably wider than its author could have expected. Thus, in the course of time the following new formulations have been given: under identical conditions a) equal volumes of solutions contain equal numbers of solute molecules (Avogadro-van't Hoff law), b) equal volumes of solutions contain equal number of ions of strong electrolytes (Avogadro-Arrhenius law).

In its application to gases the strict formulation of the law is: equal volumes of gases at the same temperature and at equal infinitesimally low pressures contain equal numbers of molecules (Avogadro-Berthelot law).

3. The analogy between a molecular gas and an electron gas in the volume of an ion of ideal spherical form (an eight-electron ion of inert-gas configuration) makes it possible to give a new formulation to Avogadro's law which is supported by the available experimental data: under identical conditions two ions of equal volumes contain equal numbers of electrons.

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*In Russian.
**Russian translation.

ADSORPTION OF TOLUENE-HEPTANE MIXTURES
ON SILICA GELS AND CARBON BLACKS

A. V. Koselev, V. V. Khopina, and Iu. A. El'tekov *

The extent to which hydrocarbons are adsorbed depends on the structure of the hydrocarbon molecule itself, the nature and structure of the adsorbent, the composition of the solution, and the temperature. The study of the adsorption of hydrocarbons from liquid mixtures is therefore of great theoretical interest; it is also of great practical importance, as it should aid in the development of methods of adsorptional-chromatographic separation of complex mixtures of hydrocarbons. The literature [1-8] on the adsorption of liquid hydrocarbon mixtures and their chromatographic separation has been surveyed in reviews [9, 10], and we shall not discuss it here. In these investigations the effect of the structure of the adsorbent on the extent of adsorption has not been studied; in the main, only finely porous silica gel has been used in the adsorption investigations.

The present paper forms a continuation of our series of papers on adsorption from liquid mixtures of hydrocarbons [9, 11, 12] and is devoted to a study of the adsorption of toluene from its solutions in heptane on silica gels of various structures. This system is recommended by many authors [4, 6, 13, 14] for the determination of the specific surfaces of catalysts and adsorbents.

EXPERIMENTAL

Silica Gels. We used three silica gels: coarsely porous silica gel KSK-1, silica gel T which had a somewhat irregular porosity, and finely porous silica gel KSM-2. KSK-1 was purified by treatment with nitric acid vapor and repeated washing with 1 : 3 hydrochloric acid and distilled water. The conditions for the washing of KSM-2 are given in [15]. Silica gel T was not washed. The surface area of the coarsely porous KSK-1 was determined in the investigation [16] by the adsorption of methanol and in the investigation [11] by the adsorption of benzene vapor and of phenol from its solutions in heptane; it was 340 sq.m/g. The surface areas of the non-uniformly porous T [16] and the finely porous KSM-2 [15] were determined by the adsorption of methanol and nitrogen, respectively. The structural characteristics are given below in the table.

Hydrocarbons. Toluene and heptane were purified by distillation through a column: toluene had d^{20}_4 0.8656; $n^{20}D$ 1.4950; and b.p. 110-111° (748mm); heptane had d^{20}_4 0.6837; $n^{20}D$ 1.3885; and b.p. 97.8-98.2° (754mm).

Measurement of Adsorption from Solution. A known volume (v = 5 ml) of a solution of known volume concentration c^0_2 was poured into a tube containing a known weight (m = 2-3g) of silica gel. The tube was sealed and was shaken in a thermostat until adsorption equilibrium was attained. The equilibrium concentration c_2 was then determined. The adsorption was determined from the usual formula,

$$x^{(v)}_2 = \frac{v(c^0_2 - c_2)}{m},$$

(1)

which gives the excess of toluene in the adsorption space as compared with its content in an equal volume of equilibrium solution [9]. Concentrations of solutions were determined by means of an interferometer with the aid

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* A. L. Kliachko-Gurvich also participated in the work.

of a calibration curve [17]. The calibration curve was determined for concentrations ranging from pure heptane to pure toluene, i.e. up to $c_2 = 1/v_2 = 9.4$ moles/liter (v_2 = molar volume of toluene). In the high concentration range the scale of the compensator may not be sufficiently long for substances whose refractive indices differ greatly. In this case a shorter cell is used, or a supplementary curve is plotted with a standard solution or another liquid. We used a cell in the form of a wedge in which layers of solution down to 1 mm in thickness could be examined; with this a calibration curve could be determined without standard solutions for concentrations from 0 to 3 moles/liter. For the plotting of the calibration curve in the concentration range 3-7 moles/liter, cyclo-hexane was taken as standard liquid. In this concentration range the calibration curve was determined only over certain intervals, namely 2.0-4.8, 5.6-6.6, 7.6-8.0, and 8.6-9.4 moles/liter, which made it possible to economize in the hydrocarbons without reducing the accuracy of the adsorption determination. On each of such sections of the isotherm, several points were determined.
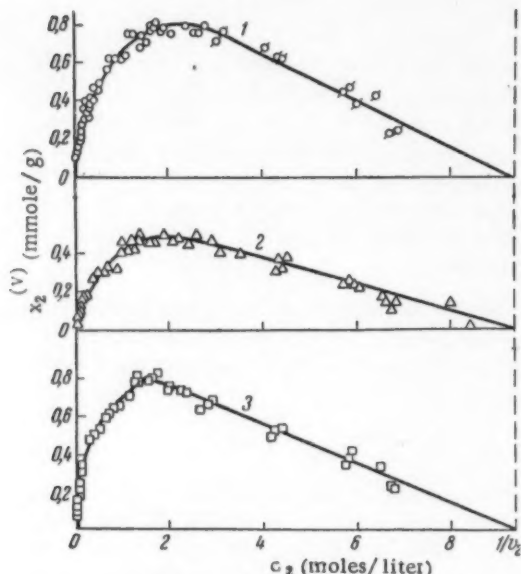
Fig. 1. Experimental isotherms for the adsorption of toluene from its solutions in heptane: 1) on KSK-1; 2) on T; 3) on KSM-2 (o - points obtained by A. L. Kliachko-Gurvich)

Experimental Adsorption Isotherms. Fig. 1 shows our isotherms for the adsorption of toluene from its solutions in heptane at 20° on silica gels of various structures, calculated for 1 g; i.e. curves for $x_2^{(v)}$ against c_2. Fig. 2 shows the initial sections of these curves on a larger scale. It will be seen from Fig. 1 that in this case the isotherms of these components, which are mutually soluble in all proportions, pass through a maximum; also, toluene is positively adsorbed over the whole concentration range, in accordance with the enhanced energy for adsorption on silica gel found in aromatic hydrocarbons, which form π-complexes with surface hydroxyls of silicic acid [9, 12, 18, 19]. At high concentrations there is an almost linear fall in the adsorption.

Absolute Adsorption Isotherm for Coarsely Porous Silica Gel. In order to compare the results with a view to the determination of the effect of reduction in pore size and in order to compare them with data in the literature on adsorption from toluene-heptane and other binary hydrocarbon solutions, adsorption must be expressed in absolute units $\Gamma_2^{(v)} = \dfrac{x_2^{(v)}}{s}$, i.e. must be calculated per unit adsorbent surface s.

The absolute isotherm for the adsorption of toluene from its solutions in heptane can be obtained for KSK-1, because in this case the surface determined from the adsorption of methanol vapor is accessible also for the adsorption of larger molecules [11]. The absolute isotherm obtained in this way for KSK-1 is given in Fig. 3. The maximum value of $\Gamma_2^{(v)}$ is 2.4 μ moles/sq.m, which corresponds to almost complete displacement of heptane from the silica gel surface. With further increase in concentration the surface is still more compactly filled with toluene. In this case, as in the case of the adsorption of benzene [11], the thickness of the adsorption layer of toluene can be determined from the slope of the descending section of the isotherm by use of the formula:

$$\tau = -\left(\frac{\partial \Gamma_2^{(v)}}{\partial c_2}\right)_{a_2 \to a_{2\infty}},$$

(2)

in which a_2 is the total toluene content of the adsorption layer and $a_{2\infty}$ is the limiting value of this when the adsorption layer is completely filled with toluene [9]. The value then obtained for τ is 3.7 A, which is indeed equal to the van der Waals thickness of the benzene ring. Hence, when adsorbed from heptane solution onto silica gels, toluene is oriented parallel to the surface of the silica gel; adsorption remains unimolecular, and τ remains constant.

Fig. 2. Initial sections of experimental isotherms for the adsorption of toluene from its solutions in heptane: 1) on KSK-1; 2) on T; 3) on KSM-2
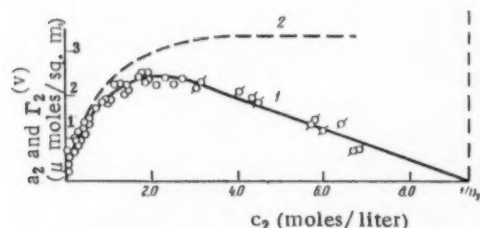
Fig. 3. Absolute isotherms for the adsorption of toluene from its solutions in heptane on KSK-1: 1) the adsorption $\Gamma_2^{(v)}$; 2) the total content a_2

The broken line in Fig. 3 is the isotherm for the total content of toluene molecules in the adsorption volume, as calculated from the formula:

$$\alpha_2 = \Gamma_2^{(v)} + \tau c_2. \qquad (3)$$

From this isotherm we determined the limiting value $a_{2\,\infty} \approx 3.3$ μmoles/sq.m and area occupied by a toluene molecule on a silica gel surface in a compact adsorption layer $\omega_0 = 50$ A^2. This value corresponds to a flat orientation of the toluene molecules on the silica gel surface, and it exceeds the corresponding value for benzene by about 10 A^2 [11] •

Adsorption from solutions is determined by the difference in the molecular fields of the adsorbent and the solution. In general form, the relationships of a_2 and $\Gamma_2^{(v)}$ of Component 2 to its concentration in the solution are given by the following equations [20] ••:

$$\alpha_2 = \frac{\tau K c_2}{1 + (K-1)\, v_2 c_2}; \quad \Gamma_2^{(v)} = \frac{\tau K c_2}{1 + (K-1)\, v_2 c_2} - \tau c_2,$$

$$(4,5)$$

in which v_2 is the molar volume of this component, and the equilibrium constant K is related to the corresponding expressions for the chemical potentials or mean potential energies of the components of the solution in the absorption layer ψ_2^s, ψ_1^s and in the bulk of the solution ψ_2, ψ_1:

$$K = e^{-\frac{(\psi_2^s - \psi_1^s) - (\psi_2 - \psi_1)}{RT}} = e^{-\frac{\Delta}{RT}}, \qquad (6)$$

Hence, the equilibrium constant for adsorption from solutions is determined by the total change in mean potential molar energies of the components for their mutual displacement in the surface layer and in the bulk of the solution. For non-ideal solutions Δ depends on the concentration. If one of the components is adsorbed strongly, i.e. if ψ_2^s differs greatly from ψ_1^s as in the case of the adsorption of aromatic hydrocarbons on silica gel, then the departure from ideality in the bulk of the solution, i.e. the difference between ψ_2 and ψ_1, plays a subordinate part and $\Gamma_2^{(v)}$ is always positive. If however, ψ_2^s is very close in value to ψ_1^s, then the departure from ideality plays a determining part. In this last case it is impossible to make direct inferences concerning the isotherms for the adsorption of the components from liquid mixtures on the basis of the adsorption properties of the pure components. In this case the value of Δ will depend greatly on concentration and it may change its sign. Correspondingly, the quantity K-1 in Equations (4) and (5) may become negative, and the relationship between $\Gamma_2^{(v)}$ and c_2 will be very complex. For the investigation of this matter it is essential to have information concerning activities in the surface and bulk solutions.

• This value $\omega_0 = 50$ A^2 is considerably higher than the usually used value of 34 A^2, which is calculated from the density of the liquid by the BET equation; the BET equation is obtained on the basis of the hypothesis of spherical symmetry of adsorbate molecules.

•• These equations are analogous to those of Semenchenko [21] for adsorption at a solution-gas interface.
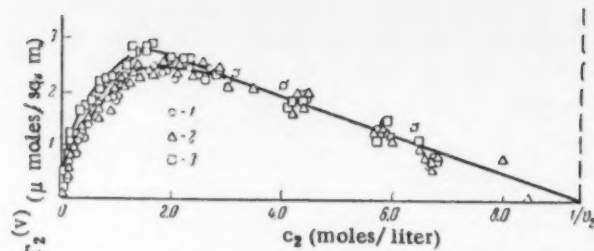
Fig. 4. Scale adjustment of experimental results on the adsorption of toluene from its solutions in heptane to the absolute isotherm on KSK-1: 1) absolute isotherm; 2) isotherm on T; 3) isotherm on KSM-2
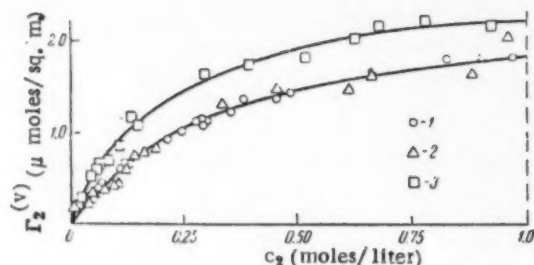
Fig. 5. Initial sections of the isotherms for the adsorption of toluene from its solutions in heptane which are represented in Fig. 4 (numbering of the curves as before)
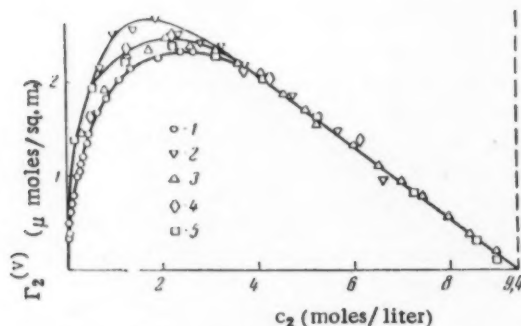
Fig. 6. Scale adjustment of isotherms for the adsorption of toluene by silica gels from solutions in heptane to the absolute isotherm for KSK-1: 1) absolute isotherm; 2) according to [5]; 3) according to [7]; 4) according to [6]; 5) according to [8]

The effect of the structure of the silica gel on the adsorption of toluene from its solutions in heptane can be judged from a comparison of the absolute isotherm obtained on coarsely porous silica gel (Fig. 3) with adsorption isotherms for the more finely porous silica gels. Fig. 4 shows the results of a scale adjustment of our experimental adsorption isotherms for T and KSM-2 to the absolute isotherm obtained for coarsely porous KSK-1. The adjustment coefficient [22] enables us to estimate the surface accessible for the absorption of toluene molecules; in the case of finely porous silic gels this surface is less than that determined from the adsorption of nitrogen and methanol vapors, because part of the surface of the fine pores that is accessible to nitrogen and methanol molecules is inaccessible to the large molecules of toluene. The values of these surfaces are given below. It will be seen from Fig. 4 that the adjusted isotherm for T is in close fit in all concentration ranges with the absolute isotherm for the adsorption of toluene from its solutions in heptane on coarsely porous KSK-1.

The adjusted adsorption for toluene on the more finely porous KSM-2 rises more rapidly in the initial region. The steeper rise of the isotherm for adsorption on the finely porous silica gel is seen more clearly in Fig. 5, which shows the initial sections of these isotherms. In this case the effect of the narrowing of the pores is analogous to that observed previously for the adsorption of benzene from its solutions in heptane [11] on silica gels of various structures. In the reduction of pore size from 104 A (KSK-1) to 38A (KSM-2) the maximum of the isotherm moves in the direction of lower concentrations (from 2.0 to 1.5 moles/ liter). According to Semenchenko's molecular theory of adsorption [21], the shift in the maximum here indicates increase in adsorption potential *.

In Fig. 6 we compare the absolute and scale-adjusted isotherms for the adsorption of toluene from solutions in saturated hydrocarbons on various silica gels, obtained from our experiments and calculated by us from the data of other authors [5-8]. The method of calculation is given in [9]. We carried out the scale adjustment [22] of the experimental isotherms obtained in the investigations [5-8] to our absolute isotherm for the adsorption of toluene on coarsely porous KSK-1 in the region of the linearly falling section of this isotherm. It will be seen from

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* The increase in the adsorption potential of toluene is probably due to the formation of a larger number of π -complex bonds when aromatic molecules are drawn into the finer pores.

Fig. 6 that here again we find that in the initial region there is a steeper rise in the isotherms for finely porous silica gels corresponding to the increased adsorption potential of the fine pores. The values of the surfaces of these samples as determined by the method of adjusting the toluene adsorption isotherms to our absolute isotherm are less than those obtained from the adsorption of vapors*, as will be seen from the table.

TABLE

Specific Surfaces of Silica Gels determined from the Adsorption of N trogen and Methanol Vapors and Estimated by the Method of Scale Adjustment of Isotherms for the Adsorption of Toluene from its Solutions

Silica gel sample	Pore size d (A)	Specific surface $\underline{s}$ (sq. m/g)	
		from adsorption of nitrogen and methanol vapors	from adsorption of toluene from its solutions
KSK-1 [11]	104 (nonuniform porosity)	340	340
T [24]		267	200
KSM-2 [15]	38	370	290
KSM-1 [16]	33	555	440
Silica gel [8]	21	800	665
Silica gel [7]	---	793	687
Silica gel [6]	18	780	670

In the investigations [5-8, 13] isooctane was used as solvent instead of heptane, but the replacement of heptane by isooctane has little effect on the adsorption of toluene because heptane and isooctane molecules are absorbed on silica gel about equally and extremely feebly.

Comparison of Adsorption Isotherms for Various Binary Hydrocarbon Solutions on Silica Gel. The comparison of the absolute adsorption isotherms of various binary hydrocarbon solutions on silica gels is of great interest. In Fig. 7 we compare our calculated absolute adsorption isotherms for various hydrocarbon mixtures on silica gels. From Fig. 7 we derive the following sequence of aromatic and unsaturated hydrocarbons with respect to tendency to be adsorbed from solution in saturated hydrocarbons. Benzene is adsorbed better than toluene, but worse than naphthalene [24], which is in accordance with the fact that the π-electron density, calculated for the area occupied by a molecule, is greater for naphthalene and less for toluene than for benzene. We then have the isotherm for the adsorption of cyclohexene from its solutions in hexane, calculated by us from data in [3]. The adsorption isotherm for the monoolefin 1-hexene from its solutions in heptane, calculated from Mikhailova's data [10], lies below that for the corresponding cycloolefin, cyclohexene: the total area of 1-hexene molecules is greater (an edge-on orientation of the molecules is possible for cyclohexene), and the numbers of double bonds capable of forming π-complexes with silicic acid are identical. The reduction in the absolute values of $\Gamma_2^{(v)}$ shows that in the case of these olefins there is no longer such a complete displacement of saturated hydrocarbon from the silica gel surface as in the case of benzene and toluene. However, in the case of the adsorption of binary mixtures of components having similar adsorption properties, such as hexane and cyclohexane [2] or heptane and methylcyclohexane [2], the extent of adsorption is very small and the isotherms lie close to the concentration axis and intersect it near the middle, i.e. the adsorption changes sign because of the importance of changes in the molecular field of a liquid with change in concentration in cases of weak adsorption.

Comparison of the Adsorption of Toluene from its Solutions in Heptane on Silica Gel and on Carbon Blacks. In Fig. 8 we compare absolute isotherms for adsorption from heptane solutions at 20° on coarsely porous silica gel KSK-1 and on two carbon blacks: channel carbon degassed at 800° and having an acidic surface**, and carbon graphitized at 1700° in a stream of hydrogen [12]. On the carbon with the acidic surface toluene was absorbed

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* With regard to the difficulties met in the estimation of the surfaces of finely porous adsorbents from the adsorption of vapors see [23].

** This sample adsorbed caustic alkali from aqueous solutions to the extent of 0.2 milliequiv./g.
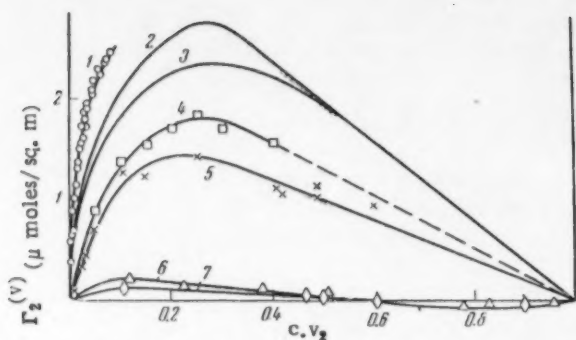
Fig. 7. Comparison of absolute isotherms for adsorption on silica gel from binary hydrocarbon solutions: 1) naphthalene-heptane; 2) benzene-heptane; 3) toluene-heptane; 4) cyclohexene-hexane; 5) 1-heptene-heptane; 6) heptane-methylcyclohexane; 7) hexane-cyclohexane

Fig. 8. Absolute isotherms for the adsorption of toluene from its solutions in heptane: 1) on KSK-1; 2) on oxidized carbon; 3) on graphitized carbon

positively over almost the whole of the concentration range, but the extent of adsorption on the carbon was considerably lower than on the silica gel. This may be explained by the fact that in the case of silica gel there is, on the one hand, a considerably greater supplementary effect of the acid-base type between the toluene molecules and the surface and, on the other hand, a considerably lower adsorption energy for the solvent (heptane) on silica gel. In the case of the graphitized sample, the removal of surface oxides has a marked effect on the extent of the adsorption of toluene from its solutions in heptane. In this case the positive adsorption of toluene at low concentrations is reduced and passes through zero at c_2 = about 4 moles/liter; at high toluene concentrations it attains high negative values. This indicates the considerable positive adsorption of heptane from its solutions in toluene on graphitized carbon. The standard heat of adsorption of heptane vapor on graphitized carbon is 14.0 kcal/mole [25], whereas the standard heat of adsorption of toluene vapor is 12 kcal/mole [26]. The areas ω_0 occupied by heptane and toluene molecules in a compact monolayer are fairly close to one another. All this creates conditions for the preferential adsorption of heptane. However, in the first half of the range of toluene concentrations it is nevertheless toluene, and not heptane, that is positively adsorbed from these solutions on graphitized carbon. This is associated with the characteristic of adsorption from liquid solutions noted above, namely the mutual displacement of components not only in the adsorption layer, but also in the bulk phase. An important part is played here by change in the molecular field in the bulk of a liquid solution; for a more precise interpretation of this phenomenon, therefore, it is necessary to have information on the departures of toluene-heptane solutions from the ideal laws.

SUMMARY

1. Adsorption isotherms were determined for toluene adsorbed from its solutions in heptane on silica gels of various porous structures. The thickness of a unimolecular adsorbed layer of toluene is 3.7 A; toluene molecules are oriented in the flat position with respect to the silica gel surface.

2. Reduction in the pore size of silica gel from 104 to 30 A, which increases the adsorption potential, increases also the extent to which toluene is adsorbed at low concentrations and brings about a shift in the maximum of the isotherm in the direction of lower concentrations for more finely porous samples.

3. The preferential adsorption of aromatic and unsaturated hydrocarbons on silica gel from their solutions in saturated hydrocarbons is associated with two factors: the magnitude of the interaction between the aromatic nuclei and the hydroxyls of silicic acid, and the effect of substituents, which increase the total area occupied by the molecule on the silica gel surface and weaken adsorption on an acidic surface.

4. On a carbon black with an acidic surface toluene is adsorbed positively over the whole range of concentrations from its solutions in heptane, but it is adsorbed more weakly than on silica gel. The graphitization of carbon black greatly reduces the adsorption of toluene, and the adsorption becomes negative at high toluene concentrations.

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*In Russian.
**Original Russian pagination. See C. B. Translation.

DIELECTRIC POLARIZATION OF MOLECULAR COMPOUNDS OF IODINE AND BROMINE

V. M. Kazakova and Ia. K. Syrkin

The anomalous properties of the "brown-violet" and "brown" solutions of iodine (in C_6H_6, C_5H_5N), e.g. enhanced solubility and reactivity, have been investigated with the aid of ultraviolet absorption spectra and have been explained on the view of the existence of complexes between iodine and solvent molecules in these solutions. It has been suggested that the bond between the components in the molecular complex is of a donor-acceptor nature (iodine as acceptor and solvent as donor), and such complexes have been called "charge-transfer" compounds. This hypothesis has received strong support from experiments in numerous recent investigations of the ultraviolet absorption spectra of iodine solutions carried out under various conditions: at ordinary temperatures, at high pressures, at the temperature of liquid nitrogen, and in many solvents, e.g. hydrocarbons, aromatic amines, alcohols, and nitriles.

It has long been known that the solutions of iodine in certain solvents begin to conduct electricity after a time. Measurements of the polarization of iodine in various solvents showed that it is higher in the brown solutions than in the violet [1]. Thus, in benzene the polarization of iodine P = 39 cc, which corresponds to a dipole moment of $\mu = 0.6$ D (in the violet solutions in cyclohexane P = 31 cc and $\mu = 0$), in cyclohexane P = 56 cc, which corresponds to $\mu = 1.1$ D. There is a still greater increase in polarization in the case of the interaction with dioxane and pyridine [2], and this can be explained by the formation of a new donor-acceptor bond between iodine and the other component of the complex.

There is little information in the literature on the interaction of bromine with organic substances. This is possibly to be explained by the fact that the investigation of intermolecular action and the formation of molecular compounds is most usually done by spectrum methods. Bromine is an extremely reactive substance and readily gives substitution products with many organic compounds, particularly in the light. The molecular compound formed by bromine with dioxane $C_4H_8O_2 \cdot Br_2$, is well known: it has been isolated in the free state and characterized. There is also a bromine compound of pyridine $C_5H_5NBr_2$. These molecular compounds are used in the bromination of unsaturated hydrocarbons [3].

The absorption spectra of solutions of bromine in aromatic hydrocarbons (benzene and its alkyl derivatives) have been investigated [4]. It was shown that the interaction of bromine with hydrocarbons is much weaker than that of iodine. It was of interest to investigate the ability of bromine to form molecular compounds with other classes of substances, the molecules of which contain atoms with unshared pairs of electrons and are able to exhibit donor properties. Because of the difficulty of investigating the absorption spectra of such systems, it is desirable to use other sensitive methods. Such methods include the measurement of dielectric polarization, for it is known that the formation of molecular compounds is accompanied by considerable changes in total polarization. Thus, in the case of dioxane dibromide [2] the experimental value of the dielectric polarization exceeds the value calculated by additivity by 35 cc. We studied the interaction of iodine and bromine with many nitrogen- and oxygen-containing organic compounds in solution by the dielectric-polarization method and investigated the abilities of bromine and iodine to form molecular compounds.

EXPERIMENTAL

The dielectric polarization of the interacting substances was determined in benzene solution at concentrations ranging from 0.05 to 0.001 expressed as mole fractions; it was calculated from the equation.

$$\frac{\epsilon-1}{\epsilon+2}\cdot\frac{\sum\limits_{i=1}^{i=n} M_i f_i}{d} = \sum\limits_{i=1}^{i=n} P_i f_i = P,$$

in which ϵ is the dielectric constant of the solution, M. is the molecular weight, $\underline{d}$ is the density, $\underline{f}$ is the mole fraction, and P is the total polarization. The dielectric constants of the solutions were measured by the beat method at 25°. The densities of the solutions and of benzene were measured by the pycnometer method.

All the substances investigated were carefully purified by methods described in the literature [5]. As the measurements were carried out at very low concentrations of the solutes, much attention was given to the degree of purity of the solvent. The experimental values of dielectric polarization were extrapolated graphically to infinite dilution ($f_2 = f_3 = 0$). The polarization values for the substance interacting in benzene obtained by extrapolation were compared with the values calculated on an additivity basis, and the value of the discrepancy

$$\Delta P = \Sigma P_{expt} - \Sigma P_{add}$$

served as a measure of the interaction between the components.

TABLE

No.	System	Range of $(f_2=f_3)\cdot 10^{+5}$	Range of (P_2+P_3)expt(cc)	(P_2+P_3)extrap (cc)	(P_2+P_3)add(cc)	ΔP_{extrap} (cc)	μ of org.cpd.(D)	Lower limit of μ of mol.cpd. (D)
1	4-Picoline + I_2	439—648	824—893	780	218	562	2.68	5.87
2	Quinoline + I_2	104—465	500—615	485	172	313	2.10	4.45
3	Acridine + I_2	244—432	363—387	360	193.5	166.5	1.98	3.51
4	Piperidine + I_2	86,0—139	1110—822	(1350)	100	(1250)	1.29	(7.90)
5	Triethylamine + I_2	96,0—163	1450—1174	(1850)	86	(1764)	0.83	(9.30)
6	Anipyrine + I_2	66,0—120	1246—1228	1245	719	526	5.47	7.45
7	8-Quinolinol + I_2	119—241	296—269	320	244	76	—	—
8	Azobenzene + I_2	125—288	107—113	106	103.5	2.5	—	—
9	Cinnamic acid + I_2	129—477	135—129	140	139	1	—	—
10	Diethyl ether + I_2	246—521	131—118	130	90	40	—	—
11	Thiophene + I_2	179—525	81,4—71	80	71	9	—	—
12	Pyridine + Br_2	262—3090	693—645	660	145	515	2.22	5.45
13	4-Picoline + Br_2	715—1444	825—797	790	197	593	2.68	5.98
14	Quinoline + Br_2	217—534	735—702	751	151	600	2.10	5.80
15	Acridine + Br_2	121—463	403—500	385	172.5	212.6	1.98	3.76
16	Azobenzene + Br_2	220—353	108—144	90	82.5	7.5	—	—
17	Cinnamic acid + Br_2	201—526	104—94	105	103	2	—	—
18	Diethyl ether + Br_2	1258—1635	114—105	134	69	65	—	—
19	Thiophene + Br_2	140—322	61,7—70,9	70	50	20	—	—
20	Aniline + nitrobenzene	1519—25 895	411—221	—	417—262	from 0 to 41 cc	—	—

No.	System	Range of f_2 naphthalene	Range of f_2 (halogen)10^5	Range of f_2 P_3 expt(cc)	P_{true} (cc)	Range of ΔP (cc)
21	Naphthalene + I_2	10 415—5 853	73.0—130	49—54	31	18—23
22	Naphthalene + Br_2	9 137—2 778	222—458	32—35	17.7	14.3—17.3

The table gives experimental values of the dielectric polarizations of substances dissolved in benzene over the investigated concentration range, the departures of these from the additive-basis values, and lower limits for the dipole moments of the molecular compounds formed. The polarizations of these systems were determined at low concentrations of interacting substances $f_2 = f_3 = 0.001$-0.050). This was necessary mainly because the compounds formed, being highly polar, are poorly soluble in benzene. Moreover, the use of low concentrations reduced the chance of the occurrence of chemical reactions between the components.

Values of the polarizations of systems for which the dependence of polarization on concentration is very marked are given in parentheses. The measurements showed that iodine gives highly polar molecular compounds with 4-picoline, quinoline, acridine, piperidine, triethylamine, and antipyrine. It is known that in all these compounds nitrogen is at the negative end of the dipole. The highly polar antipyrine is an exception. Comparison of the dipole moment of antipyrine with those of its derivatives indicates that both nitrogens of antipyrine carry partial positive charges. The valence state of nitrogen changes considerably in the molecular compounds of these bases. This can be seen by comparing values of ΔP and μ for the molecular compounds of iodine with pyridine [2] and with 4-picoline:

$$C_5H_5N \cdot I_2 \qquad \Delta P = 260 \, cc \qquad \mu = 4{,}17 \, D$$
$$CH_3C_5H_4N \cdot I_2 \qquad \Delta P = 562 \, cc \qquad \mu = 5{,}87 \, D$$
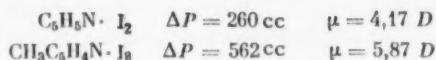
As already stated above, the dielectric polarizations of the solutes were extrapolated graphically to $f_2 = f_3 = 0$. Hence, the values of dipole moments calculated under these conditions must be regarded as lower limits of the actual values, because an equilibrium exists between the compound AD and its components A and D:

$$AD \rightleftharpoons A + D$$

and for the calculation of the true value of the dipole moment of the compound AD it is necessary to take the equilibrium constant into account.

In the case of systems with high values of ΔP it may be expected that the equilibrium will be greatly displaced to the left and the values given for the dipole moments will be close to the true values. Comparison of ΔP values for molecular compounds of iodine with pyridine, quinoline, and acridine shows that the donor properties of these aromatic bases fall into the following order: quinoline > pyridine > acridine. This order is not the same as that of the basicities.

Of the bases investigated the strongest was piperidine, which gave a very polar compound with iodine which was very sparingly soluble in benzene (measurements were therefore made at $f_2 \leqslant 0{,}0015$). The most powerful donor was found to be triethylamine. In the case of the interaction of triethylamine with iodine the effect of "reversal" of moment is less and the increase in polarization is considerably greater than in the case of pyridine, 4-picoline, quinoline, and acridine, in which nitrogen carries a considerable negative charge. Antipyrine was the most polar of the compounds investigated. The value of ΔP for the molecular compound of iodine with antipyrine was less than for the compounds with piperidine and triethylamine, but greater than for compounds with aromatic bases. This indicates that the nitrogen atoms of the five-membered antipyrine ring acquire to some extent the properties characteristic of the conjugation present in aromatic bases. Azobenzene (trans-isomer) is a nonpolar compound. The two nitrogens form part of a conjugated system with the two benzene rings. The presence of such a conjugated chain has the result that both nitrogens are very weak donors.

With iodine, 8-quinolinol gives a polarization that departs only very slightly from that calculated on an additive basis. This is explained by the presence of an internal hydrogen bond in the 8-quinolinol molecule. It is probable that the unshared pair of electrons of the nitrogen of 8-quinolinol interacts to some extent with the hydrogen of the hydroxyl, so that the nitrogen no longer has appreciable donor activity toward iodine.

For the system diethyl ether $+ I_2$ the value of ΔP is very low, which indicates the weak donating power of oxygen, as compared with nitrogen. The sulfur of thiophene has still weaker donor properties. It might be thought that sulfur would be a stronger donor than oxygen, for the "onium" state is much more readily attained in sulfur than in oxygen. In thiophene, however, the sulfur occupies a special position because of its conjugation with the carbons of the ring; as a result, the thiophene is fairly stable, even in chemical respects.

For the system naphthalene $+ I_2$ the increase in polarization is greater than for benzene $+ I_2$, which is in accord with Korthüm's results [6] for this system in cyclohexane. In the case of the system cinnamic acid + iodine there is practically no increase in polarization. From this, however, we cannot infer unequivocally that cinnamic acid does not interact with iodine at all, because the interaction of I_2 with the double bond of cinnamic acid may be of the same order as its interaction with benzene.

Bromine, like iodine, gives strongly polar molecular compounds with pyridine, 4-picoline, quinoline, and acridine, which is shown by the considerably enhanced polarization found by experiment, as compared with that calculated on an additivity basis. In view of the high reactivity of bromine in the systems formed by pyridine, quinoline, and acridine with bromine, experiments were carried out to determine whether any chemical reaction occurs in the course of 1-2 hours after the preparation of the solutions by the titration method. The experiments showed that almost all of the bromine is in solution in the chemically uncombined state.

The large increase in the polarization of compounds of bromine with 4-picoline, as compared with the case of pyridine, can be explained in the same way as in the case of iodine. The donor properties of these bases fall into the same order as for molecular compounds of iodine. Comparison of the values of μ and ΔP for molecular compounds of bromine and iodine with these bases leads to the conclusion that bromine has stronger acceptor properties than iodine in the interaction with these substances and gives compounds of greater polarity. This is in accord with the electronegativities (according to Mulliken) of these elements: Br, 418 kcal; I, 382 kcal. Further confirmation of the very powerful acceptor properties of bromine is to be found in the fact that we did not succeed in investigating the systems of bromine with triethylamine and with piperidine even in the concentration range $f_2 = f_3 = 0.0003 - 0.0005$, because, even in such dilute solutions, the compounds formed were immediately precipitated quantitatively as yellow solids. This can be explained on the view that the compounds formed are highly polar and almost insoluble in benzene. The high polarities of molecular compounds of bromine and iodine with pyridine, quinoline, and acridine are due to due to some dissociation into ions:

$$\text{NI}^+ + \text{I}^- \quad \text{and} \quad \text{NBr}^+ + \text{Br}^-$$
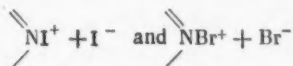
This phenomenon is revealed in the investigation of the electrical conductivity of solutions of iodine-pyridine in organic solvents [6]. The electrical conductivity increases with time, though it increases very slowly, so that changes are noticeable only from several days after the preparation of the solutions. In the investigation of the absorption spectra of solutions of iodine in pyridine and quinoline [7], after 2-3 weeks absorption bands were observed which were probably to be attributed to products of the substitution of iodine in the rings of the bases.

In view of this it may be supposed that substitution in pyridine, quinoline, and acridine rings may proceed in several stages: 1) the formation of the highly polar molecular compounds described above, irrespective of the medium in which the reaction proceeds; this stage of the reaction is almost instantaneous; 2) the dissociation of the molecular compounds into ions; the rate of this stage depends on the medium; 3) the formation of nuclear-substitution products of the bases. If we suppose that bromination proceeds through these stages, then the positively charged nitrogen in the ions $(C_5H_5NBr)^+$ and $(C_9H_7NBr)^+$ should orient bromine into the 3,5 positions of pyridine and the 3,6 positions of quinoline, which is confirmed by experiment.

Apart from systems formed from bromine and aromatic bases, we investigated systems formed by bromine with various other substances. For the system azobenzene + Br_2 there is scarcely any discrepancy in the polarization, the effect being almost additive. The value of ΔP at concentrations of $f_2 = 0.0020-0.0035$ is 30-40 cc, and the extrapolated value is close to that based on additivity. This indicates that the compound formed dissociates very readily into its components on dilution. There are references in the literature to interaction between diethyl ether and bromine. The existence of the compound $(C_2H_5)_2O \cdot Br_2$, m.p. $-40°$, has been proved. We measured polarizations for the system diethyl ether + Br_2 and obtained a value of ΔP of 65 cc. Oxygen passes much less readily into the onium condition and is a weaker donor than nitrogen. Moreover, the compound $(C_2H_5)_2O \cdot Br_2$ is very unstable in solution and decomposes into its components. With thiophene, bromine, like iodine, shows no appreciable interaction.

We measured the polarizations of the systems cinnamic acid + Br_2 and naphthalene + Br_2 in benzene with the object of verifying the power of the double bond to form π-complexes. With cinnamic acid bromine gives dielectric polarizations that scarcely differ from the values calculated on an additivity basis, and there is no reason to suppose that stable π-complexes are formed. In the polarization measurements on naphthalene + Br_2 the naphthalene was taken not in equivalent amount, but in excess, in order to shift the equilibrium toward the formation of the molecular compound. The increase in the polarization of this system was 15 cc, i.e., less than that for iodine and naphthalene (about 21 cc); this indicates that bromine is weaker than iodine as an acceptor in interactions with hydrocarbons; this is in accord with the literature.

The system aniline + nitrobenzene in benzene is somewhat removed from the other systems investigated. We considered it to be of interest to investigate this system because of the following considerations. It is known that traces of nitrobenzene color aniline brown, although pure aniline and pure nitrobenzene are colorless. This phenomenon gave us reason to suppose that aniline forms a molecular compound with nitrobenzene. Measurements showed that there is only a slight reduction in total polarization and at low concentrations there is almost exact additivity. Nitrobenzene molecules associate strongly even at low concentrations. This is indicated by the sharp reduction in the polarization of nitrobenzene in benzene with increase in the concentration of $C_6H_5NO_2 \cdot B$. In pure nitrobenzene the effective orientation polarization is 61.5 cc, instead of 329 cc in dilute solutions. It is possible that nitrobenzene molecules associate with formation of quadripoles, which arrange themselves in parallel planes. In aniline the interaction of the molecules is weaker. The effective orientation polarization of pure aniline is 30.5 cc, and in dilute solutions it is about 49 cc. It is probable that the association of nitrobenzene molecules is retained to a considerable extent in solution in admixture with aniline. The aniline molecules may arrange themselves above the upper and below the lower planes of the associated nitrobenzene molecules. Such an arrangement of the molecules leads in strong solutions to some reduction in the total polarization. The very small change in polarization gives us reason to suppose that no stable hydrogen bonds are formed between aniline and nitrobenzene molecules.

SUMMARY

1. Dielectric polarizations were measured for 22 ternary systems of iodine and bromine (acceptors) with various organic compounds (donors) in benzene as solvent.

2. On the basis of the departures of the experimental values of the polarization from the values calculated on an additivity basis, inferences were made about the interaction between the components.

3. In some cases we detected the formation of stable molecular compounds of high polarity, due to the donor-acceptor bond.

4. In interactions with nitrogen-containing compounds the stronger acceptor is bromine, and in interactions with aromatic hydrocarbons the stronger acceptor is iodine.

5. The sequence of the donor properties of the bases investigated does not coincide with the sequence of their basicities.

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*Original Russian translation. See C.B. Translation.

PASSIVATING PROPERTIES OF PIGMENTS

I. L. Rozenfel'd, F. I. Rubinshtein. and V. V. Zhebrovskii

On the modern views of the electrochemical mechanism of corrosion processes, the part played by film-forming substances and pigments must be regarded from the point of view of the effect that they have on the kinetics of electrode reactions determined by the corrosion process. This process can be suppressed either by strong inhibition of the anodic reaction of ionization of the metal and of the cathodic reaction of the reduction of oxygen, or by the inclusion in the system of a great resistance having feeble ionic and electrode conductivity.

The protection of metals from corrosion by the application of paints can in principle be effected in two ways:

a) by mechanical isolation of the metal from the corrosive medium;

b) by the retardation of electrode reactions that determine the corrosion process.

The first method can be effective only when the coating isolates the metal completely from the action of the medium. For this purpose it must be impervious to water, oxygen, and ions of other electrolytes. Comparison of data on the permeability of various films to oxygen and water with the amount required for the occurrence of the corrosion process at the normal speed shows that these agents reach the metal surface in sufficient amount, so that limitation of diffusion cannot inhibit the corrosion process effectively [1]. Moreover, under the action of the external medium the isolating properties of the coatings deteriorate with time. When protection on this basis is used, any damage to the coating or increase in its porosity favors the development of corrosion.

The second method (electrochemical) is the most effective because it does not require that the metal must necessarily be isolated completely from the external medium. For the operation of the electrochemical mechanism it is necessary that the film should contain components capable of changing the kinetics of electrode reactions determining the corrosion process and by doing so completely suppress this process. The functions of such components may be fulfilled by pigments introduced into paint coatings. Pigments can exert their protective properties by polarizing the metal either cathodically or anodically and so bringing the metal into a passive state. In cathodic protection, by dissolution of the pigment the potential of the base metal is shifted to a negative value such that the anodic reaction of ionization of the metal is completely suppressed. For this it is necessary that electrons should be fed continuously to the iron; this can be ensured by the use of metallic pigments so long as the metal of the pigment is more negative than iron and the pigment particles are in metallic contact with metal to be protected. It is on this principle that the coatings containing zinc dust as pigment, recently introduced into Great Britain and other countries, are based. The content of zinc dust in the coating must be 95% on the amount of binder. The action of such coatings continues until the dissolution of the protecting metal is complete; any further action of the film is due merely to mechanical isolation of the metal.

In anodic passivation, the pigment, which has oxidizing properties or is able to form sparingly soluble compounds with the metal being protected, isolates a considerable part of the metal and creates an exceptionally high current density in the pores of the protective films. The potential of the metal therefore moves to such a value that the passage of ions from the metal lattice to the solution becomes impossible and only the formation of phase or adsorption layers on the electrode can proceed.

Some inhibiting pigments, e.g. red lead, have basic properties and form soaps with the binders, which, in presence of water or oxygen, create dispersed mixtures that protect the metal from corrosion. Other pigments, which have some solubility in water, act as oxidants. Such pigments include zinc and strontium chromates, and the mixed barium-potassium chromate. The anions of such pigments react with the surface of the metal and form

adsorption or phase films that protect the metal from corrosion. It is assumed that chromate ions are absorbed on iron with saturation of the free valences of the metal surface, because of this specific adsorption, the reactivity of the surface layer of atoms in the metal lattice falls sharply [2].

It is clear that the protective properties of pigments must depend on their solubility, ability to send ions having passivating properties into the solution, and ability to maintain the oxidation-reduction potential of the system at a high level for a long time. In other words, the protection is determined to a considerable extent by the composition and properties of the aqueous extracts obtained by the action of water or other electrolytes on the pigments.

Scarcely any study has yet been given to the passivation of metals by means of pigments, and this makes it impossible to analyze the mechanism of the corrosion of metals under paint films. The object of our investigation was the study of the passivating properties of pigments that have oxidizing properties.

<center>EXPERIMENTAL</center>

The following pigments were investigated: zinc chromate (22.0% CrO_3, 58.6% ZnO), strontium chromate (48.5% CrO_3), mixed barium-potassium chromate (38.3% CrO_3, 4.6% $BaSO_4$, 1.6% CaF_2, 1.6% SiO_2, 0.6% Fe_2O_3, 1.2% $CaCO_3$, 0.2% MgO, 0.5% MnO_2, and 0.13% Na_2O), and a mixed barium-potassium chromate (45% CrO_3) obtained from chemically pure reagents. In this series of experiments the metal used was Mark 45 steel.
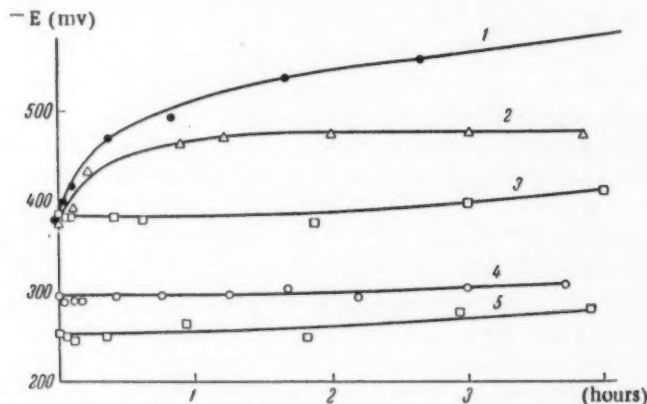
Fig. 1. Electrode potentials of steel in aqueous extracts of various pigments (content of pigment in suspension = 40%):
1) distilled water; 2) zinc chromate; 3) strontium chromate; 4) mixed barium-potassium chromate (chemically pure); 5) mixed barium-potassium chromate (technical)

We used the procedure of the electrochemical investigations of atmospheric corrosion developed at the Institute of Physical Chemistry of the Academy of Sciences of the USSR [3]. We studied the irreversible electrode potentials of steel in thin layers (165 μ) of aqueous extracts obtained by the action of water on various pigments. The aqueous extracts were obtained at various ratios of weight of pigment to weight of water. The aqueous suspensions were kept for ten days at 23-25°; the filtrate was then filtered off, and the filtrate was investigated.

Fig. 1 gives the curves for the change of potential in the aqueous extracts of various pigments for a pigment content in the suspension of 40%. It will be clearly seen from the curves that the irreversible potential of steel in the aqueous extract depends greatly on the nature of the pigment. The steel acquires its most positive potential in an extract of the technical mixed barium-potassium chromate; this is followed by the extract of chemically pure barium-potassium chromate, and next comes the extracts from strontium chromate and zinc chromate.

CrO$_3$ (g/liter)
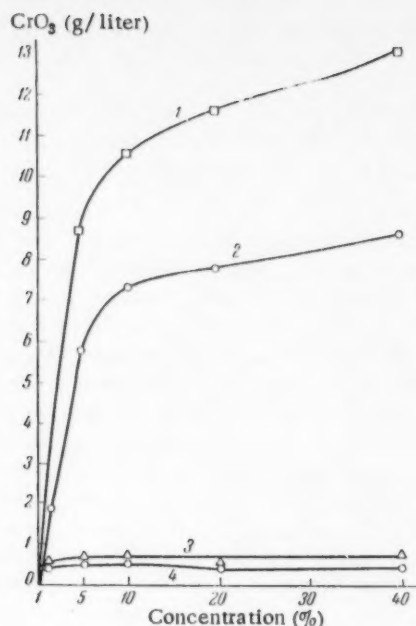
Fig. 2. Relation of the CrO$_3$ content of
aqueous extracts of pigments to the pigment
content of the suspension:
1) mixed barium-potassium chromate (tech-
nical); 2) mixed barium-potassium chromate
(chemically pure); 3) strontium chromate;
4) zinc chromate

The potential of steel in water that does not contain
the soluble components of the pigments is 200-300 mv
more negative than the potentials established on
steel in aqueous extracts of the pigments. The poten-
tial of steel in absence of pigments becomes much more
negative in the course of time, which is to be explained
by the destruction of the natural oxide film and by par-
tial concentrational polarization by oxygen. In the ex-
tracts containing soluble compounds of the pigments,
particularly of the mixed barium-potassium chromate,
the potential of the steel assumes a stable value. This
fact and the large shift in the potential toward the pos-
itive region provide convincing proof that the protec-
tive effects of pigments are associated with the passivat-
ing properties of extracts obtained by the action of the
water that penetrates the film. The highest oxidizing
power is possessed by aqueous extracts of the mixed
barium-potassium chromate. This pigment will almost
certainly be more effective than strontium and zinc
chromates.

It was evident that the passivating properties of
aqueous extracts of the pigments were associated with
the presence of chromate ions in the solution. Hence,
in order to determine the causes of the different behav-
iors of the different pigments it was of interest to study
the concentrations of chromate ions in the different
aqueous extracts and also their dependence on the rela-
tive weights of pigment and water. For this purpose all
the extracts were analyzed for CrO$_3$ content. The rela-
tion of the CrO$_3$ contents of aqueous extracts of the pigments to the pigment contents of the suspensions is shown
in Fig. 2. The curves in Fig. 2 show that the solubilities of zinc and strontium chromates do not depend greatly
on the pigment content and that on the average they amount to 0.5 g/liter, calculated as CrO$_3$. The mixed barium-
potassium chromate contains much more water-soluble material than zinc and strontium chromates, and this en-
sures a relatively high concentration of chromate ions in the extracts (8-13 g/liter).

The powerful passivating properties of mixed chromates observed in the study of irreversible potentials must
thus be associated with the high solubilities of barium-potassium chromates and the creation of a high oxidation-
reduction potential. However, it must not be concluded that we must try to prepare a pigment of maximum sol-
ubility. Such a pigment would soon lose its power and could not send chromate ions into the solution for a long
time. It is evident that the pigment must have some minimum solubility that ensures a sufficiently high concen-
tration of chromate in the extract and also the ability to act for a long time. In this respect the solubilities of
zinc and strontium chromates are clearly insufficient and would have to be raised. As will be shown below, there
are methods of doing this. With increase in the pigment content the amount extracted from the mixed barium-
potassium chromate increases, and the most pronounced rise in the curve is observed with rise in pigment content
up to 10%, after which the CrO$_3$ content of the extract, though still rising, rises much less sharply. The extent to
which CrO$_3$ passes into solution from the technical barium-potassium chromate is greater than in the case of the
analogous pigment prepared from chemically pure materials. This gives us reason to suppose that the ease with
which chromate ions can be washed out of pigments may be increased by the introduction of other components,
which either form more soluble compounds or have an indirect effect on the solubility. We have verified this
method for the case of zinc chromate.

In the aqueous extract of the mixed barium-potassium chromate (technical) the potential became more
positive than in the extract from the same pigment prepared from chemically pure materials. This is associated
with the higher concentration of chromate ions in the extract of the technical chromate and confirms the con-
clusion that various additions favor increase in the content of passivator in the aqueous extract.

Fig. 3. Electrode potentials of steel in aqueous extracts of the mixed barium-potassium chromate (hemically pure) for various contents of the pigment in water:
1) 1% of pigment; 2) 10% of pigment; 3) 40% of pigment

Fig. 4. As Fig. 3, but for technical chromate

Comparing the potentials in a potassium chromate solution containing 0.5 g/liter of CrO_3 with those in aqueous extracts of zinc and strontium chromates containing the same amounts of CrO_3, we must conclude that the passivating properties of pigments are to be attributed not only to the CrO_3 content, but also to some extent to the presence of other compounds in the aqueous extracts.

The passivating properties of pigments must depend greatly on the amount of water that will wash the pigment, because this is related to the chromate content of the extract passivating the metal surface. In Figures 3 and 4 we show the relation of the electrode potential of steel to the relative weights of pigment and water for mixed barium-potassium chromate (technical and chemically pure). From the curves in Fig. 3 it will be seen that at high dilution (1% of pigment) the aqueous extracts do not possess strong passivating properties and the potential of the steel becomes more negative with time. As the dilution is reduced, i.e. as the pigment content of the suspension is increased, the passivating properties of the extracts are greatly improved as a result of their increased contents of chromate ions, and the potential of the steel becomes more negative and more stable with time. It follows that, although films containing passivating pigments may be pervious to water, for the development of the maximum passivating effect of the mixed barium-potassium chromate it is necessary that the permeability of the paint film to vapor should be as low as possible so as to ensure a relatively high concentration of the passivator in the aqueous extract at the metal surface.

SUMMARY

1. The passivating properties of chromate pigments were studied. The irreversible electrode potential of steel in thin layers of aqueous extracts of pigments was displaced by 200-300 mv toward the positive region and became extremely stable with time.

2. The potential of steel is greatly dependent on the nature of the pigment. In passivating power the chromate pigments fall into the following series: mixed barium-potassium chromate (technical) ≻ mixed barium-potassium chromate (chemically pure) ≻ strontium chromate ≻ zinc chromate.

3. It was shown that the great differences in the passivating properties of the pigments are due to the differences in the solubility of the passivating parts of the pigments. The CrO_3 concentration in the extract of a mixed chromate is considerably greater than in extracts of strontium and zinc chromates (10-13 g/liter instead of 0.5 g/liter).

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INVESTIGATION OF ELECTROPHILIC AND HOMOLYTIC SUBSTITUTIONS
AT A CARBON ATOM BY THE METHOD OF ISOTOPIC EXCHANGE

O. A. Reutov

In the course of an investigation of the mechanism of electrophilic and homolytic substitutions at a saturated carbon atom for the case of organomercury compounds [1-6] we used the isotopic-exchange method. As the results then obtained were of interest on their own account, we made a systematic study of isotopic-exchange reactions of the following types:

$$R - Hg - R + \overset{\bullet}{H}g \rightleftarrows R - \overset{\bullet}{H}g - R + Hg;$$
$$R - Hg - X + \overset{\bullet}{H}g \rightleftarrows R - \overset{\bullet}{H}g - X + Hg;$$
$$R - Hg - X + \overset{\bullet}{H}gX_2 \rightleftarrows R - \overset{\bullet}{H}g - X + HgX_2;$$
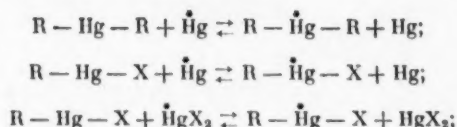
(R = Ar, Alk, or ClCH = CH; X = Cl or Br; the radioactive mercury isotope Hg^{203} was used).

Depending on the character of the radical, these reactions are substitutions at saturated, olefinic, or aromatic carbon atoms. Some results of this study are reported in the present paper.

Symmetrical organomercury compounds of the aromatic series react in an unexpected way with finely divided mercury under extremely mild conditions [7]. The rate of the isotopic-exchange reaction
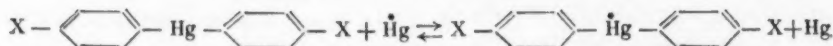
is substantially dependent on the character of X (see figure).

It will be seen from the figure that the rate of this isotopic-exchange reaction increases as the substituent X is varied, the following sequence being found:

$$O_2N, Cl < H < CH_3 < OCH_3.$$

The accuracy* of our experiments does not yet enable us to establish which of the two organomercury compounds, bisnitrophenylmercury and bischlorophenylmercury, reacts more rapidly with mercury. It is notable that isotopic exchange proceeds under very mild conditions. Bismethoxyphenylmercury, for example, reacts fairly rapidly with mercury, even in the cold**. In benzene at 20° (concentrations: bismethoxyphenylmercury 0.05 mole/liter; mercury 0.87 mole/liter) equilibrium is established in 16 hours.

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* Here and later the reproducibility obtained in duplicate experiments on heterogeneous reactions is within ± 10% on the average.

** In contrast with the case of organomercury compounds, the analogous isotopic exchange reaction of organoantimony compounds [8]

$$Ar_3Sb + Sb^{124} \rightleftharpoons Ar_3Sb^{124} + Sb$$

proceeds at an appreciable rate only at temperatures of above 160°.

Under such mild conditions it would appear to be impossible for this reaction to proceed by a free-radical mechanism, e.g.

$$Ar_2Hg \rightleftarrows 2Ar\cdot + \cdot Hg\cdot$$
$$2Ar\cdot + \cdot \overset{\bullet}{Hg}\cdot \rightleftarrows Ar_2\overset{\bullet}{Hg},$$
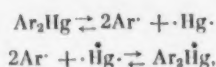
Evidence against the free-radical mechanism is provided also by the results on the isotopic exchange of the unsymmetrical diarylmercurys:
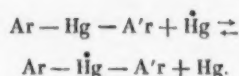
$$Ar - Hg - A'r + \overset{\bullet}{Hg} \rightleftarrows$$
$$Ar - \overset{\bullet}{Hg} - A'r + Hg.$$

If the reaction proceeds through the stage of the formation of the free radicals $Ar^\bullet$ and $A'r^\bullet$, then, after the establishment of isotopic equilibrium in the reaction mixture, Ar-Hg-A'r should be accompanied by the compounds Ar_2Hg and $A'r_2Hg$. Actually, however, as was shown in the case of (p-nitrophenyl) phenylmercury, when isotopic equilibrium is established only the original unsymmetrical compound is present.
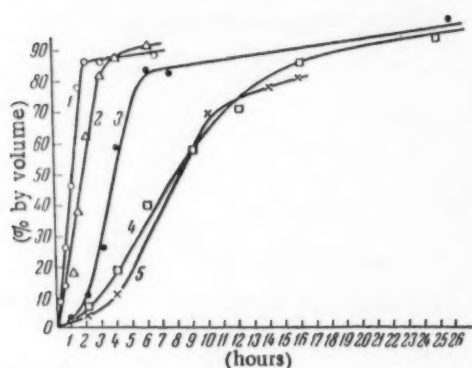
Relationship between the rate of isotopic exchange* and the character of X: 1) $(CH_3OC_6H_4)_2Hg$ $(X = CH_3O)$; 2) $(CH_3C_6H_4)_2Hg$ $(X = CH_3)$; 3) $(C_6H_5)_2Hg$ $(X = H)$; 4) $(ClC_6H_4)_2Hg$ $(X = Cl)$; 5) $(NO_2C_6H_4)_2Hg$ $(X = NO_2)$ In all cases the experiments were carried out under the same conditions (in pyridine at $60 \pm 0.1°$; concentration of organomercury compound 0.028 mole/liter; 50 fold excess of mercury (measured in equivalents); standard vigorous stirring)

Hence, the homolytic isotopic-exchange reaction under consideration is not a free-radical reaction; it occurs directly between diarylmercury molecules and metallic mercury, probably through the transition state (A):

$$Ar-Hg-Ar + \cdot \overset{\bullet}{Hg}\cdot \rightleftarrows Ar \overset{Hg}{\underset{Hg}{\cdots}} Ar \rightleftarrows Ar-\overset{\bullet}{Hg}-Ar + \cdot Hg\cdot$$
$$(A)$$
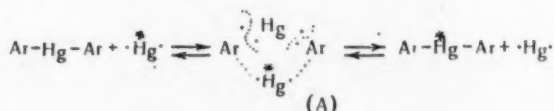
From the way in which the substituent X affects the rate of the isotopic-exchange reaction, it may be presumed that increase of the electron density on the carbon atoms at which substitution occurs facilitates the formation of the transition state (A).

Like arylmercurys, arylmercury chlorides readily undergo isotopic-exchange reactions with radioactive mercury:

$$X - \langle\!\!\!=\!\!\!\rangle - Hg - Cl + \overset{\bullet}{Hg} \rightleftarrows$$
$$\rightleftarrows X - \langle\!\!\!=\!\!\!\rangle - \overset{\bullet}{Hg} - Cl + Hg.$$
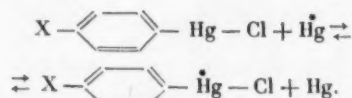
As in the case of diarylmercurys, electropositive substituents (X) accelerate and electronegative substituents retard the isotopic-exchange reaction. All arylmercury chlorides react more rapidly with mercury than the corresponding diarylmercurys. It should be noted that in this case a free-radical mechanism is still less probable, because arylmercury chlorides do not decompose with formation of free radicals even when their solutions are exposed to ultraviolet radiation.

In the study of the reaction of aliphatic and alicyclic organomercury salts with mercury it was found that only α-mercurated carbonyl compounds react under mild conditions (in benzene in the cold) [9]. Below we give the formulas of the organomercury salts, and in Table 1 we give the results of their isotopic-exchange reactions with mercury.

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* In all cases the extent of exchange is expressed as a percentage of the equilibrium value.

(I) cyclohexanone with =O and HgBr

(II) $C_6H_5-CH-COOC_2H_5$, with HgBr below

(III) $C_6H_5-CH-COOC_{10}H_{19}$ with HgBr below

(IV) C_6H_5-HgBr

(V) bicyclic structure with =O, $CH_2C_6H_5$, HgBr

(VI) bicyclic structure with =O, HgBr

(VII) $ClHg-CH_2-C\lessgtr^O_{OC_3H_7}$

(VIII) bicyclic structure with =O, HgCl

(IX) bicyclic structure with HgBr

(X) $CH_3-CH_2-CH_2-CH_2-HgBr$

It follows from Table 1 that the reactivities of α-mercurated carbonyl compounds toward mercury fall in the follow sequence: 2-(bromomercuri)cyclohexanone (I) > ethyl (bromomercuri)phenylacetate (II) > (L)-menthyl (bromomercuri)phenylacetate (III) > phenylmercury bromide (IV) > 3-benzyl-3-(bromomercuri)camphor (V) > 3-(bromomercuri)camphor (VI) > propyl (chloromercuri)acetate (VII) > 1-(chloromercuri)camphenilone (VIII).

It will be seen that the reactivity is determined not only by the electronic character of the groups on the carbon atom attached to mercury, but in several cases also by steric factors. It is probably for this reason that (L)-menthyl (bromomercuri)phenylacetate reacts more slowly than the corresponding ethyl ester. On the other hand, when we compare the reactivities of esters of (bromomercuri)phenylacetic acid with propyl (chloromercuri)acetate

$$C_6H_5-CH-COOC_2H_5 \quad > \quad C_6H_5-CH-COOC_{10}H_{19} \quad > \quad ClHg-CH_2-C\lessgtr^O_{OC_3H_7}$$
(with HgBr below each CH)
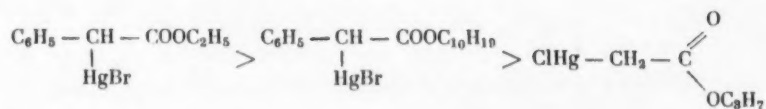
it is seen that the activating effect of the phenyl group predominates over the steric hindrance that it produces.

1-(Chloromercuri)camphenilone, like 2-(bromomercuri)camphane and butylmercury bromide, which are not α-mercurated derivatives of carbonyl compounds, does not react with mercury, even at 100° for 40 hours. The great inertness of the mercury atom in 1-(chloromercuri)-camphenilone, which is observed in many other substitution reactions, has not yet found satisfactory explanation. The reaction under consideration is probably homolytic.

In the study of symmetrization reactions of organomercury salts [10,5] it has been shown that the symmetrization agent (KI, NH$_3$) does not attack the R-HgX molecule, but combines with HgX$_2$ formed as a result of the reversible reaction

$$2R-HgX \rightleftarrows R-Hg-R + HgX_2,$$
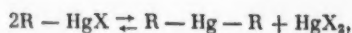
It is therefore natural to examine whether such an equilibrium plays a determining part in our case. We may, in fact, represent the possible mechanism of the isotopic-exchange reaction under consideration as follows:

a) $2R-HgX \rightleftarrows R-Hg-R + HgX_2$;

b) $HgX_2 + \overset{\bullet}{Hg} \rightleftarrows \overset{\bullet}{Hg}X_2 + Hg$;

c) $R-Hg-R + \overset{\bullet}{Hg}X_2 \rightleftarrows R-\overset{\bullet}{Hg}X + R-HgX$.
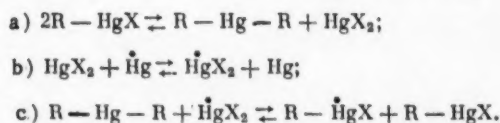
TABLE 1

Results of Isotopic Exchange of Organomercury Salts with Mercury*

Experiment	Organo-mercury compound	Exchange (%) in a time (hours) of												
		0.5	1.0	2.0	3.0	4.0	5.0	6.0	6.5	10.0	14	15	20	40
1	(I)	—	81	98	99									
2	(II)	16	51	83	91	98	100							
3	(III)	2	8	45	66	76			84	93				
4	(IV)										51			
5	(V)											39		
6	(VI)												17	
7	(VII)					0							0	
8	(VIII)												0	0
9	(IX)												0	0
10	(X)													0

* In each experiment the concentration of organomercury compound was 0.015 mole/ liter; the excess of mercury (in equivalents) was 66-fold in Experiments 1-3 and 132-fold in Experiments 4-10; the solvent was acetone in Experiment 4, dioxane in Experiment 6, and benzene in the remaining experiments.

However, such a scheme is not in accord with two experimental facts. The first of these is that some organomercury salts react with mercury under milder conditions than with mercuric halide. Thus, ethyl (bromo-mercuri)phenylacetate and benzylmercury chloride readily react with $\overset{\bullet}{Hg}$ in organic solvents in the cold, but do not react with HgX_2 under these conditions. The second fact is that we could not detect the formation of even traces of mercurous halide in any of the cases studied, whereas, if reaction proceeded through the equilibrium (a), then not only symmetrical organomercury compound, but also some mercurous halide would be obtained as a result of the reaction:

$$Hg + HgX_2 \rightarrow Hg_2X_2.$$
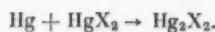
The homolytic isotopic-exchange reaction under consideration is unlikely to be a free-radical reaction because it proceeds in the cold under conditions under which no decomposition of organomercury compounds with formation of free radicals has ever been detected. Evidence against the formation of free radicals as chemically independent particles is provided also by the fact that isotopic-exchange proceeds with preservation of the stereochemical configuration at the carbon atom attached to mercury. The reaction mechanism, therefore, can probably be represented by the following scheme:

$$R-Hg-X + \overset{\bullet}{Hg} \;\rightleftharpoons\; R\overset{Hg}{\underset{\overset{\bullet}{Hg}}{\cdots\cdots}}X \;\rightleftharpoons\; R-\overset{\bullet}{Hg}-X + Hg'$$
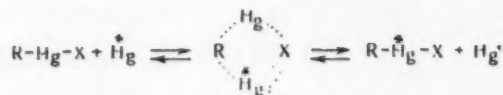
We studied also [11] the isotopic exchange of organomercury salts (I-X, see scheme) with mercuric halide labeled with Hg^{203}. It was found that, with the exception of (VIII), the organomercury salts that are α-mercurated carbonyl compounds react with mercuric halide under mild conditions:

$$R - HgX + \overset{\bullet}{Hg}X_2 \rightleftarrows R - \overset{\bullet}{Hg} - X + HgX_2.$$
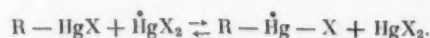
TABLE 2

Results of Isotopic Exchange of Organomercury Salts with Mercuric Halide[*]

Experiment	Organo-mercury compound	Exchange (%) in a time (hours) of											
		1	2	3	4	5	6	7	8	12	15	20	36
1	(I)										97		
2	(I)		94										
3	(V)										95		
4	(V)		95										
5	(II)						0					0	
6	(II)	22	40	56	67				99			0	
7	(III)						0					0	
8	(III)		5	6			17		20				
9	(III)						42						
10	(III)	16	27	36	43								
11	(VI)									38			52
12	(VIII)											0	
13	(IX)											0	
14	(IX)											0	
15	(X)											0	
16	(X)											0	

[*] In all experiments equimolecular amounts of organomercury salt and mercury halide were taken. The concentration of each reactant was 0.015 mole/liter in Experiments 1-5, 7, 9, 12-16, 0.02 mole/liter in Experiment 11, 0.05 mole/liter in Experiment 8, and 0.1 mole/liter in Experiments 6 and 10. The solvent was benzene in Experiments 1, 3, 5, 7, 8, 13, and 15, acetone in Experiments 2, 4, 6, 9, 10, 14, and 16, dioxane in Experiment 11, and ethanol in Experiment 12. Experiments 1,3,5,7,13, and 15 were carried out at 23°, Experiments 2,4,8,9,11,14, and 16 at 50°, Experiments 6 and 10 at 53°, and Experiment 12 at 75°.

The experimental results are given in Table 2, from which it can be seen that the reactivity of organomercury salts toward mercuric halide diminishes in the following order: 2-(bromomercuri)cyclohexanone (I), 3-benzyl-3-(bromomercuri)camphor (V) > ethyl (bromomercuri)phenylacetate (II) > (-)-menthyl (bromomercuri) (L)-phenylacetate(III) > 3-(bromomercuri)camphor (VI) > 1-(chloromercuri)camphenilone (VIII), 2-(bromomercuri)camphane (IX), butylmercury bromide (X).

Comparison of the rates of reaction of the various organomercury salts with mercury and with mercuric halide shows that no notable difference in the effects of structural factors on the rates of the homolytic (with $\overset{\bullet}{Hg}$) and electrophilic (with HgX_2) reactions is to be observed.

The isotopic exchange of organomercury salts with mercuric halide is accelerated by bases.

Thus, isotopic equilibrium between benzylmercury bromide and $H\overset{\bullet}{g}Br_2$ (concentration of each 0.028 mole/liter) in toluene containing 20% of diethylamine is established in three hours at 98.4°. In absence of diethylamine the reaction does not go at all. Pyridine has a similar effect. It may be considered that the effect of bases is associated with the solvation of the mercury atom by the base, as a result of which the carbon-mercury bond is weakened:

667
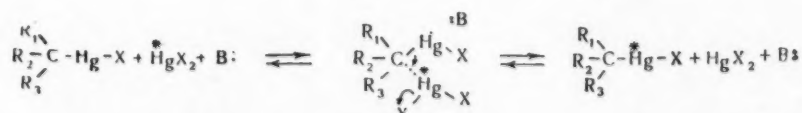
In the case of α-mercurated carbonyl compounds the isotopic-exchange reaction is accelerated also by acids. The catalytic effect of acids is probably associated with the action of the proton of the acid on the oxygen of the carbonyl group, which must also result in weakening of the carbon-mercury bond:

$$-\overset{|}{\underset{\underset{HgX}{|}}{C}}-C\overset{O}{\underset{}{}} + H-A \rightleftarrows -\overset{|}{\underset{\underset{HgX}{|}}{C}}-C\overset{O\cdots H-A}{\underset{}{}}-$$
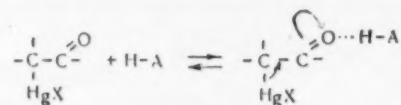
On the basis of the reaction between cis- and trans-2-methoxycyclohexylmercury chlorides and $\overset{\bullet}{Hg}Cl_2$ it was shown that this isotopic-exchange reaction, like other electrophilic substitutions [3, 5, 12], proceeds with preservation of stereochemical configuration at the carbon atom affected.

Substitution at an olefinic carbon was studied for the case of the chlorovinyl compounds of mercury. Nesmeianov and Borisov [14], who studied exchange of metal in stereoisomeric organometallic compounds of the type

$$\underset{H}{\overset{R}{>}}C = C\underset{M}{\overset{H}{<}} \quad \text{and} \quad \underset{R}{\overset{H}{>}}C = C\underset{M}{\overset{H}{<}},$$
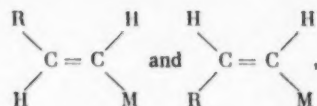
established that electrophilic and homolytic exchange reactions at an olefinic carbon proceed with preservation of the geometric configuration. This rule was proved on the basis of a large amount of experimental material mainly by the indirect method of "even and odd cycles".

By the use of the isotope method in the present work we obtained direct proof of the correctness of this rule [13]. As examples of electrophilic reactions we studied the reaction of trans- and cis-2-chlorovinylmercury chlorides with mercuric chloride labeled with radioactive mercury Hg^{203}. The reaction was carried out in acetone solution in the cold. In both cases we showed that isotopic equilibrium is established rapidly (in less than five minutes) and that the original stereochemical configuration of the chlorovinyl group is preserved completely:

1) $\underset{H}{\overset{Cl}{>}}C = C\underset{HgCl}{\overset{H}{<}} + \overset{\bullet}{Hg}Cl_2 \rightleftarrows \underset{H}{\overset{Cl}{>}}C = C\underset{\overset{\bullet}{Hg}Cl}{\overset{H}{<}} + HgCl_2$

2) $\underset{Cl}{\overset{H}{>}}C = C\underset{HgCl}{\overset{H}{<}} + \overset{\bullet}{Hg}Cl_2 \rightleftarrows \underset{Cl}{\overset{H}{>}}C = C\underset{\overset{\bullet}{Hg}Cl}{\overset{H}{<}} + HgCl_2$
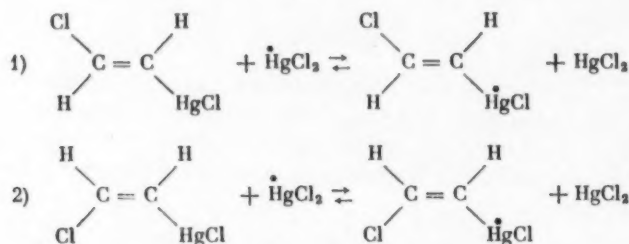
As examples of homolytic reactions we studied the reaction of mercury labeled with Hg^{203} with trans- and cis-2-chlorovinylmercury chlorides and also with bis-trans- and bis-cis-2-chlorovinylmercurys. All four organomercury compounds reacted readily in acetone in the cold with finely divided mercury. Isotopic equilibrium was established in a few hours. All these reactions proceeded with strict preservation of the stereochemical configuration of the chlorovinyl group:

3) $\underset{H}{\overset{Cl}{>}}C = C\underset{HgCl}{\overset{H}{<}} + \overset{\bullet}{Hg} \rightleftarrows \underset{H}{\overset{Cl}{>}}C = C\underset{\overset{\bullet}{Hg}Cl}{\overset{H}{<}} + Hg$

4) $\underset{Cl}{\overset{H}{>}}C = C\underset{HgCl}{\overset{H}{<}} + \overset{\bullet}{Hg} \rightleftarrows \underset{Cl}{\overset{H}{>}}C = C\underset{\overset{\bullet}{Hg}Cl}{\overset{H}{<}} + Hg$

5) $$\text{(structure: } ClCH=CH\text{-}CH=CH\text{-Cl with Hg)} + \overset{\cdot}{Hg} \rightleftarrows \text{(structure)} + Hg$$

6) $$\text{(structure)} + \overset{\cdot}{Hg} \rightleftarrows \text{(structure)} + Hg$$
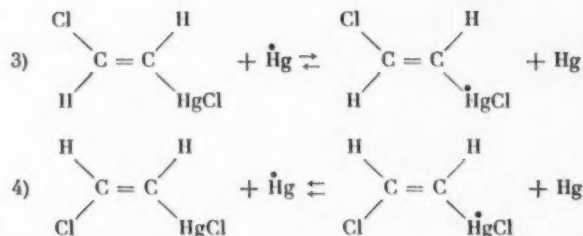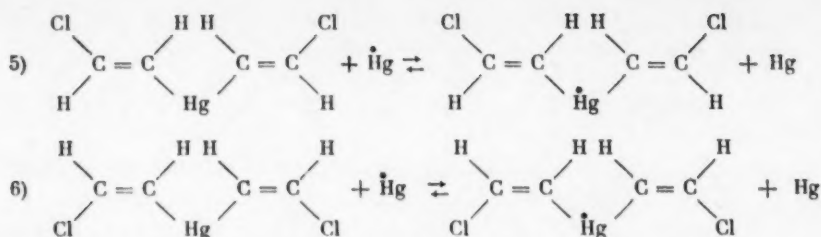
In the reaction of mercury with trans- and cis-2-chlorovinylmercury chlorides, isotopic exchange was accompanied by a side reaction in which mercurous chloride and acetylene were formed:

$$Cl - CH = CH - HgCl + Hg \rightarrow H - C \equiv C - H + Hg_2Cl_2.$$
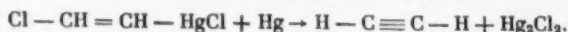
Here, therefore, we have a typical example of dual reactivity, which is so characteristic of all 2-chlorovinyl organometallic compounds.

Whereas the results of the isotopic exchange of bis-trans- and bis-cis-2-chlorovinylmercurys (Reactions 5 and 6) give direct proof of the preservation of stereochemical configuration in these reactions, the results of Reactions 1-4 are in need of further consideration.

As indicated above, the symmetrization of esters of (bromomercuri)phenylacetic acid by ammonia proceeds in two stages [5]:

a) $2R - HgX \rightleftarrows R_2Hg + HgX_2;$

b) $HgX_2 + 2NH_3 \rightleftarrows HgX_2 (NH_3)_2.$
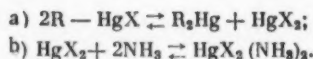
If in Reactions 1-4 an equilibrium of a similar type

$$2ClCH = CH - HgCl \rightleftarrows (ClCH = CH)_2 Hg + HgCl_2$$
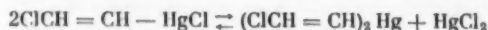
plays a part that is at all substantial, then both bis-2-chlorovinylmercury and mercuric chloride will undergo isotopic exchange with Hg and HgCl$_2$ respectively. The observed sterochemistry of Reactions 1-4 would be results of not one, but several processes. However, we showed by special experiments that bis-2-chlorovinylmercury was absent in the reaction mixture, even in the case of Reactions 3 and 4, i.e., when the excess of mercury, which would readily turn mercuric chloride into HgCl, should favor shift of the equilibrium (a) to the right with formation of appreciable amounts of the symmetrical organomercury compound. Hence, we may affirm that Reactions 1-4 do not proceed through the equilibrium, but HgCl$_2$ and Hg react directly with 2-chlorovinylmercury chlorides*. In view of this our results provide direct confirmation of the preservation of configuration at an olefinic carbon in electrophilic and homolytic substitutions.

The mechanism of the reaction of symmetrical and unsymmetrical chlorovinyl organomercury compounds with mercury is probably analogous to that of the above-considered reactions of mercury with aromatic organomercury compounds and α-mercurated carbonyl compounds.

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* In the light of these results, the view [15] that the isotopic-exchange reactions of aryl- and alkyl-mercury halides always pass through the equilibrium:

$$2R - HgX \rightleftarrows R_2Hg + HgX_2; \quad HgX_2 + HgX_2 \rightleftarrows HgX_2 + HgX_2;$$
$$R_2Hg + \overset{\cdot}{Hg}X_2 \rightleftarrows R - \overset{\cdot}{Hg} - X + R - Hg - X.$$
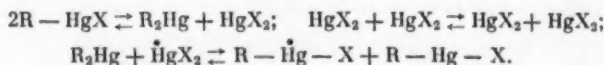
must be regarded as improbable. Organomercury salts can probably react directly with mercuric halide.

Finally, it must be pointed out that for all the isotopic-exchange reactions of R_2Hg and R-HgX with mercury studied by us it is possible to suggest yet another mechanism, based on the analogy with the readily occuring reaction between mercuric salts and mercury ($HgX_2 + Hg \rightleftharpoons Hg_2X_2$), i.e.,

$$R - Hg - X + \overset{\bullet}{H}g \rightleftarrows R - Hg - \overset{\bullet}{H}g - X \rightleftarrows R - \overset{\bullet}{H}g - X + Hg$$

and

$$R - Hg - R + \overset{\bullet}{H}g \rightleftarrows R - Hg - \overset{\bullet}{H}g - R \rightleftarrows R - \overset{\bullet}{H}g - R + Hg.$$
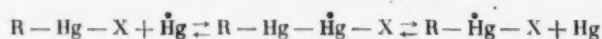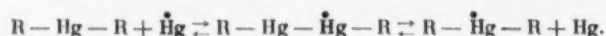
However, we consider that this mechanism is less probable for the following reasons. The Hg-X bond in the organomercury salts R-Hg-X is similar in reactivity to the Hg-X bond in the HgX_2 molecule. No substantial degree of dependence of the reactivity of the Hg-X bond in $RHgX$ on the nature of R has been observed. On the other hand, the rate of isotopic exchange between R-Hg-X and Hg depends substantially on the nature of R. If, however, we assume that the radioactive mercury enters not at the Hg-X bond, but at the R-Hg bond (with formation of R-Hg-Hg-X), then it is impossible to understand why R_2Hg should react with mercury more slowly than R-Hg-X.

The author thanks S. Z. Roginskii, Ia. K. Syrkin, and B. V. Nekrasov, Corr. Members Acad. Sci. USSR, and A. I. Brodskii, Member of the Acad. Sci. Ukrainian SSR, for discussion relating to this work.

SUMMARY

1. Diarylmercurys and arylmercury chlorides undergo isotopic exchange with mercury labeled with Hg^{203} under very mild conditions. Electropositive substituents in the para position of the benzene ring facilitate reaction, and electronegative substituents make it more difficult.

2. The homolytic reactions examined are not free-radical reactions, but proceed directly between organomercury molecules and mercury.

3. A study was made of the dependence of the rates of isotopic exchange of acyclic and alicyclic organomercury salts with mercury and with mercury chloride on structural factors and on additions of acids and bases.

4. The homolytic (with $\overset{\bullet}{H}g$) and electrophilic (with $\overset{\bullet}{H}gX_2$) isotopic-exchange reactions of organomercury salts proceed with preservation of the configuration at the saturated carbon atom.

5. By study of the isotopic exchange of 2-chlorovinylmercury compounds with $\overset{\bullet}{H}g$ and $\overset{\bullet}{H}gCl_2$, direct proof was obtained of the correctness of Nesmeianov and Borisov's rule concerning the preservation of stereochemical configuration in electrophilic and homolytic substitutions at an olefinic carbon atom.

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DECOMPOSITION OF ARENEDIAZONIUM FLUOBORATES IN BENZOIC ESTERS

L. G. Makarova and E. A. Gribchenko

In a previous communication [1] it was shown that phenyl formed in the thermal decomposition of benzenediazonium fluoborate in benzene derivatives containing orientants of the second kind (nitro, ethoxycarbonyl, and $N(Alk)_3^+$ groups) as substituents enters the benzene ring in the position meta to these groups, which proves the cationoid nature of this phenyl and the heterolytic character of the decomposition of the diazonium salt which generated it. We investigated the decomposition of benzenediazonium fluoborate in benzoic esters other than ethyl benzoate (methyl, propyl, isopropyl, and butyl benzoates) and also the decomposition of p-bromo-and p-nitro-benzenediazonium fluoborates in ethyl benzoate.

The decomposition of benzenediazonium fluoborate in methyl benzoate was carried out at 76° and 100° In both cases phenyl entered the nucleus of methyl benzoate, substitution being mainly in the meta position, though a small amount of the para isomer was also formed. The relative amounts of meta and para isomers formed were 15 : 1 at 76° and 12 : 1 at 100°. Of all the alkyl benzoates submitted to the action of benzenediazonium fluoborate, only the methyl ester gave a little of the product of para substitution in addition to the meta isomer obtained as the main product.

In the decomposition of benzenediazonium fluoborate in propyl and butyl benzoates, phenyl entered only the meta position with respect to the alkoxycarbonyl group. In addition, as in the decomposition of benzenediazonium fluoborate in ethyl benzoate, phenyl derived from the benzenediazonium salt acted on the alkoxycarbonyl group itself, and the resulting transesterification gave phenyl benzoate:

$$C_6H_5C \underset{OAlk}{\overset{O}{\|}} + C_6H_5N_2BF_4 \rightarrow \underset{\underset{Alk = n\text{-}C_3H_7,\ n\text{-}C_4H_6}{C_6H_5}}{\overset{COOAlk}{\bigcirc}} + C_6H_5COOC_6H_5$$
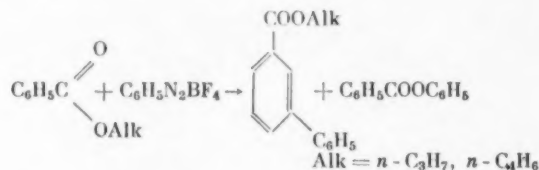
Transesterification was the sole result of the action of p-bromo- and p-nitro-benzenediazonium fluoborates on ethyl benzoate:

$$ArN_2BF_4 + C_6H_5COOC_2H_5 \rightarrow C_6H_5COOAr,$$

$$Ar \text{-} p \text{-} BrC_6H_4;\ p \text{-} O_2NC_6H_4.$$
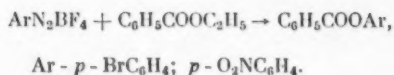
In neither case did aryl enter the benzene nucleus.

In the decomposition of benzenediazonium fluoborate in isopropyl benzoate, neither entry of phenyl into the benzene ring nor attack by phenyl on the alkoxycarbonyl group with formation of phenyl benzoate occurred. The main reaction product may have been triisopropylphenyl benzoate $C_6H_5COOC_6H_2(C_3H_7)_3$ or the benzoic esters of an alcohol $C_6H_5COOC_9H_{18}C_6H_5$, in which the structure of the skeleton of the phenol (alcohol) residue has not been elucidated. In addition, a fluoro hydrocarbon $C_{10}H_{13}F$ was found among the reaction products. The formation of these substances is probably due to the action of phenyl from benzenediazonium fluoborate on the product of the degrading, dehydrogenating, condensing, or other action of boron trifluoride (formed from benzenediazonium fluoborate) on isopropyl benzoate.

Hence, in the decomposition of benzenediazonium fluoborate in methyl, ethyl, propyl, and butyl benzoates, the phenyl derived from benzenediazonium fluoborate, unlike the phenyl formed in the decomposition of homolytically decomposing diazo compounds [2] and diaroyl peroxides [3], and from other sources [4], enters the benzene ring mainly or exclusively in the position meta to the alkoxycarbonyl group; this confirms the difference between the phenyl from benzenediazonium fluoborate and these other radicals; it confirms also its electrophilic character.

The occurrence of some, though very little, substitution in the para-position in the decomposition in methyl benzoate can be explained by the relative weakness of the alkoxycarbonyl group as a meta orientant: it is known that less than 70% of m-nitrobenzoic ester is formed in the nitration of benzoic esters [5]. Also, the transesterification of ethyl, and to a less extent also propyl and butyl, benzoate by aryl derived from arenediazonium fluoborate, for which there is no precedent in the reactions of aryl radicals from other diazo compounds on alkyl benzoates and other esters, is, as indicated previously, a proof of the decomposition of the diazonium salt that generates it.

EXPERIMENTAL

Decomposition of Benzenediazonium Fluoborate in Methyl Benzoate. Over a period of one hour with mechanical stirring 96 g (0.5 mole) of benzenediazonium fluoborate was added to 272 g (2 moles) of methyl benzoate heated to 76-78°. There were copious white fumes, and the reaction mixture gradually became dark red. When the addition was complete, stirring was continued for one hour at 80°; the mixture was then dissolved in ether, and the solution was washed with 10% sodium hydroxide solution and with water, and was dried with sodium sulfate. Ether, low-boiling substances, and methyl benzoate were distilled off, and vacuum distillation gave Fraction I (0.45 g), 158-162° (5 mm) and Fraction II (7.1 g), 167-173° (5 mm). Fraction I solidified; it was neutral to litmus; after being crystallized from ethanol it melted at 117°. The melting point of methyl 4-biphenylcarboxylate is 117° [6].

Found %: C 78.89; 78.94; H 5.82; 5.95 $C_{14}H_{12}O_2$. Calculated %: C 79.22; H 5.699

Fraction II was an oil. It was boiled with 25 ml of 30% aqueous sodium hydroxide for six hours; when the product was diluted with water it dissolved completely (the sodium salts of 4- and 2-biphenylcarboxylic acids are insoluble in water). The alkaline solution was acidified and then neutralized with sodium carbonate. The product was steam-distilled; tests with ferric chloride and bromine water for phenol in the distillate were negative. Addition of hydrochloric acid to the sodium carbonate solution gave a precipitate, which melted at 164° after crystallization from petroleum ether (b.p. 34-70°) and ethanol. The melting point of 3-biphenylcarboxylic acid is 160° [7], 166° [8]. We obtained 4 g of meta isomer and 0.26 g (calculated as biphenylcarboxylic acid) of para isomer. The results of the other similar experiments are given in the table.

Decomposition of Benzenediazonium Fluoborate in Isopropyl Benzoate. Addition of 96 g (0.5 mole) of benzenediazonium fluoborate in small portions to 164 g (1 mole) of isopropyl benzoate with mechanical stirring was commenced at 90° and continued for 90 minutes; most of the diazonium salt was added at 75-80°. The mixture was kept at this temperature for one hour. When cool the reaction mixture solidified.

It was dissolved in ether, and the solution was washed with 10% sodium hydroxide solution (acidification of the washings gave 100 g of benzoic acid) and with water; it was dried with sodium sulfate. Ether was distilled off over a water bath. Vacuum distillation then gave Fraction I (12.38 g), b.p. 55-91° (13 mm); Fraction II (10 g), b.p. 120-140° (13 mm); Fraction III (13.23 g), b.p. 160-180° (5 mm). At 220-240° (5 mm) there was decomposition and a red viscous caramel-like mass distilled over.

After redistillation Fraction I had the following constants: b.p. 157°; $n^{20}D$ 1.4712; d^{20}_4 0.9699

Found %: C 78.80; 78.90; H 8.57; 8.42; F 12.20; 11.58
$C_{10}H_{13}F$. Calculated %: C 78.91; H 8.67; F 12.48

After redistillation Fraction II had the constants: b.p. 83-84° (3 mm); $n^{20}D$ 1.4810 d^{20}_4 0.9198; weight 6 g.

Found %: C 81.81; 81.71; H 10.83; 10.67
$C_{15}H_{24}O$. Calculated %: C 81.76; H 10.98

TABLE

Decomposition of Arenediazonium Fluoborates in Alkyl Benzoates

$Ar_2N_2BF_4$		$C_6H_5COOAlk$		Reaction conditions	Reaction products	Found (%)		Calculated (%)	
Ar	Amount (g)	Alk	Amount (g)			C	H	C	H
C_6H_5	86	CH_3	272	100—110°, 2 hours	Fraction I, b.p. 160-175° (5 mm) hydrolysis → acid (3.2 g), m.p. 164° a); acid (0.27 g), m.p. 222° b); phenol c) / Fraction II, b.p. 180-220° (5 mm); precipitate (0.05 g), m.p. 117° d) filtrate after hydrolysis acid, m.p. 164° a); phenol c)				
C_6H_5	48	$n\text{-}C_3H_7$	122	80°, 2½ hours	B.p. 165-180° (8 mm) hydrolysis → acid, m.p. 164° a); phenol c)				
C_6H_5	100	$n\text{-}C_4H_9$	138	85—90°, 3 hours	Fraction I, b.p. 130-175° (5 mm) hydrolysis → benzoic acid; phenol c), Fraction II, b.p. 175-230° (5 mm) hydrolysis acid, m.p. 164° a)				
$p\text{-}BrC_6H_4$	40	C_2H_5	111	110°, 3 hours	B.p. 175-210° (5 mm), solidified, 5 g, m.p. 104-105° e,f)	56,05; 56,29	3,22; 3,09	56,34	3,27
$p\text{-}O_2NC_6H_4$	80	C_2H_5	250	130°, 5½ hours	B.p. 120-210° (4 mm), solidified, 6,3 g, m.p. 139-141° g,f); phenol c)	63,77 63,68	4,04 4,09	64,19	3,70

a) Gives no depression of melting point with known 3-biphenylcarboxylic acid. b) M.p. of 4-biphenylcarboxylic acid 222° [6], 218-219° [9]. c) Reaction with ferric chloride and with bromine water. d) Gives no depression of melting point with methyl 4-biphenylcarboxylate. e) M.p. of p-bromophenyl benzoate 104° [10]. f) Crystallized from ethanol. g) M.p. of p-nitrophenyl benzoate 142-142.5° [11].

A 0.2-g sample of the substance was treated with benzoyl chloride by the Schotten-Baumann method. The precipitate formed was washed with water and recrystallized from ethanol; m.p. 136-137.5°, undepressed in admixture with Fraction III. After recrystallization from heptane the phenylurethan of Fraction II had m.p. 177.5-178°.

Found %: C 77.23; 77.28; H 8.58; 8.54
$C_{22}H_{29}O_2N$. Calculated %: C 77.83; H 8.6

Fraction III solidified. After recrystallization from ethanol and from heptane it melted at 136.5-137.5°.

Found %: C 81.39; 81.45; H 8.85; 8.67
$C_{11}H_{14}O$. Calculated %: C 81.50; H 8.69

Found %: M 310,312
$C_{22}H_{28}O_2$. Calculated %: M 324

A 0.5-g sample of the substance was boiled for six hours with 20 ml of 10% methanolic sodium hydroxide. The methanol was distilled off, and the residue was diluted with water. The resulting alkaline solution was treated with ether, and the ether extract was washed with water and dried with sodium sulfate. After removal of ether there remained 0.2 g of oil, which was heated with 0.1 ml of phenyl isocyanate in a boiling water bath. A precipitate formed on cooling; it was crystallized from heptane and then melted, alone and in admixture with the phenylurethan obtained from Fraction II, at 177.5-178°. The alkaline solution was acidified with 15% sulfuric acid and extracted with ether; after removal of ether a solid residue remained, and after being sublimed this melted at 122°; in admixture with benzoic acid it melted at 122°.

SUMMARY

1. Phenyl formed in the decomposition of benzenediazonium fluoborate attacks propyl and butyl benzoates in the meta position, and it also brings about the transesterification of these esters; in the case of methyl benzoate it enters mainly the meta position, but some of the para isomer is formed; with isopropyl benzoate it gives a benzoic ester $C_6H_5COOC_{15}H_{24}$.

2. Transesterification is the only result of the action of aryls derived from p-bromo- and p-nitro-benzene-diazonium fluoborates on ethyl benzoate.

3. The entry of the aryl derived from an arenediazonium fluoborate in the meta position to the alkoxycarbonyl group of a benzoic ester and the transesterification of such esters by this aryl prove that the aryl is cationoid and the decomposition of arenediazonium fluoborates is heterolytic.

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COMMUNICATION 10. NEW METHOD OF SYNTHESIZING CYCLIC ESTERS OF DIALKYLSILANEDIOLS AND OF ORTHOSILICIC ACID

M. G. Voronkov, V. P. Davydova, and B. N. Dolgov

It was shown previously [1-3] that acetoxysilanes react smoothly with alcohols with formation of the corresponding alkoxysilanes and acetic acid:

$$\geq Si - OCOCH_3 + HOR \rightarrow \geq Si - OR + CH_3COOH.$$
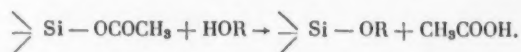
We have now investigated the possibility of applying this reaction for the synthesis of cyclic esters of dialkylsilanediols (2,2-dialkyl-1,3-dioxa-2-silacycloalkanes) by reaction between diacetoxydialkylsilanes and glycols:

$$R_2Si \overset{OCOCH_3}{\underset{OCOCH_3}{<}} + \overset{HO}{\underset{HO}{>}} (CH_2)_n \rightarrow R_2Si \overset{O}{\underset{O}{<>}} (CH_2)_n + 2CH_3COOH.$$
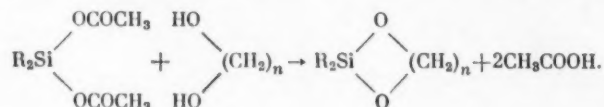
Only two cyclic esters of the above structure ($R = CH_3$, $n = 3$ and 4) have been described previously, and these were prepared by the reaction of 1,3-propanediol and 1,4-propanediol with dichlorodimethyl- or diethoxydimethyl-silane [4,5]. Attempts to prepare 2,2-dimethyl-1,3-dioxa-2-silacyclononane ($n = 6$) and 2,2-dimethyl-1,3-dioxa-2-silacyclopentane ($n = 2$) were unsuccessful [4]. In the second case the reaction product was the dimer (cf. No. 5 in the table). We found that diacetoxydialkylsilanes readily react with glycols according to the above scheme with formation in 50-70% yield of cyclic esters of dialkylsilanediols containing rings of 6-9 members ($n = 3-6$). Compounds of this type having $n = 5$ and 6 were unknown until this time, and the possibility of the existence of nine-membered rings was doubted [4].

The reaction was brought about by simple mixing of the reactants and subsequent removal by vacuum distillation of the acetic acid formed.* The cyclic ester was isolated by further vacuum distillation. The compounds prepared in this way are listed in the table.

The residue remaining after distillation of acetic acid from the mixture of diacetoxydialkylsilane and the glycol was found to consist mainly of polymer formed according to the scheme:

$$xR_2Si(OCOCH_3)_2 + xHO(CH_2)_n OH \xrightarrow{-2xCH_3COOH} [R_2SiO(CH_2)_nO]_x.$$
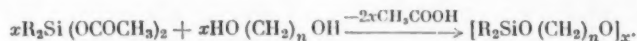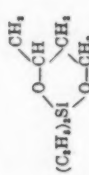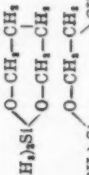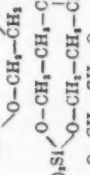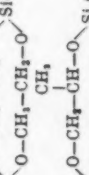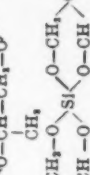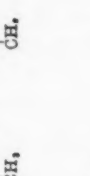
Thermal depolymerization of this polymer leads to the formation of the expected cyclic ester of the dialkylsilanediol:

$$[R_2SiO(CH_2)_nO]_x \rightleftarrows xR_2Si \overset{O}{\underset{O}{<>}} (CH_2)_n.$$

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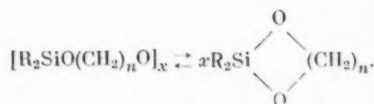
* When acetic acid was distilled off under atmospheric pressure the main reaction product was found to be the acetic ester of the glycol.

TABLE

Cyclic Esters of Dialkylsilanediols and of Orthosilicic Acid

Compound No.	Formula of compound	B.p. in C° (p in mm)	n_D^{20}	d_4^{20}	M Calculated	M Found	Found (%) Si	C	H	Calculated (%) Si	C	H	Yield (%)
1*	$(C_2H_5)_2Si\!\!<\!\!^{O-CH(CH_3)}_{\ O-CH_2}$	53,0—53,7 (7)	1,4262	0,9350	174,3	175,6 167,6	16,01 16,01	55,66 55,62	10,44 10,60	16,11	55,13	10,41	61
2	$(CH_3)_2Si\!\!<\!\!^{O-CH_2-CH_2}_{\ O-CH_2-CH_2}$	145—147 (751)	1,4222	0,9622	146,3	144,1	19,74 19,56	—	—	19,2	—	—	46
3*	$(CH_3)_2Si\!\!<\!\!^{O-CH(CH_3)}_{\ O-CH_2-CH_2}$	46—47 (8)	1,4308	0,9664	160,3	159,4 163,6	17,69 16,97	52,45 52,63	10,11 10,07	17,52	52,75	10,06	54
4*	$(CH_3)_2Si\!\!<\!\!^{O-CH_2-CH_2-CH_2}_{\ O-CH_2-CH_2-CH_2}$	65—66 (6)	1,4402	0,9660	174,3	174,3 180,3	16,04 16,04	55,22 55,40	10,46 10,41	16,11	55,13	10,41	47
5**	$(CH_3)_2Si\!\!<\!\!^{O-CH_2-CH_2-O}_{\ O-CH_2-CH_2-O}\!\!>\!\!Si(CH_3)_2$	78—80 (10)	—	—	236,4	—	23,41 23,28	—	—	23,76	—	—	70
6*	$(CH_3)_2Si\!\!<\!\!^{O-CH_2-CH-O}_{\ O-CH_2-CH-O}\!\!>\!\!Si(CH_3)_2$ $^{CH_3}_{CH_3}$	160—162,5 (761,5)	1,4300	1,0067	264,5	264,9 258,9	20,98 21,28	45,39 45,41	9,35 9,36	21,24	45,41	9,15	68
7	$CH\!\!<\!\!^{CH_2-O}_{CH_2-O}\!\!>\!\!Si\!\!<\!\!^{O-CH_2}_{O-CH_2}\!\!>\!\!CH_3 \ CH_3$	118,5 (15)	1,4412	1,1163	204,3	201,4 199,7	13,25 13,51	—	—	13,74	—	—	85

* New compound.

** M.p. 56° (from dioxane). When kept, it turns into a liquid having $n^{20}D$ 1.4380.

This reaction is reversible. Attempts to prepare five-membered dioxasilacycloalkanes by the reaction of diacetoxy-dimethylsilane with ethylene glycol and 1,2-propanediol resulted in each case in the formation of the pure dimers which are also given in the table (No. 5 and 6); when kept, these slowly polymerize in the way indicated above.

By reaction of tetraacetoxysilane with 1,3-butanediol we succeeded in obtaining a good yield of a spiro ester of orthosilicic acid, namely 2,8-dimethyl-1,5,7,11-tetroxa-6-silaspiro[5.5]undecane (No. 7 in the table), which has been synthesized previously by the reaction of $SiCl_4$ with this glycol [6]. On the other hand, the reactions of tetraacetoxysilane with 1,4-butanediol and with 1,5-pentanediol resulted merely in the formation of the acetic esters of these glycols.

EXPERIMENTAL

Commercial chemically pure glycols were taken and were vacuum-distilled immediately before use in a reaction. Diacetoxydimethyl- and diacetoxydiethyl-silanes and tetraacetoxysilane were prepared by the reaction of the corresponding chlorosilanes with acetic anhydride [1,3].

With stirring and cooling, 0.2-0.4 mole of the glycol was added to an equimolecular amount of the diacetoxy-dialkylsilane (in some cases the reaction was carried out in ether or chloroform as solvent). The mixture was stirred for two hours at room temperature, and was then vacuum-fractionated. The cyclic esters of dialkylsilane-diols obtained in this way were purified by redistillation under reduced pressure, after which their physical constants and molecular weights were determined immediately. We describe three typical experiments.

Reaction of Diacetoxydimethylsilane with 1,2-Propanediol. A mixture of 52.9 g (0.3 mole) of diacetoxy-dimethylsilane and 22.8 g (0.3 mole) of 1,2-propanediol was prepared. After the stirring treatment and the sub-sequent vacuum fractionation we obtained 26.7 g (68% of Substance No. 6 (see table), b.p. 76-79° (11 mm), which is possibly a mixture of two isomers differing in the relative positions of two of the methyl groups (4,9 and 4,10). After being purified by redistillation it had the constants given in the table. After three months in a sealed tube the molecular weight of the substance rose to 480 (476.5; 486.4), though its composition did not change.

Reaction of Diacetoxydimethylsilane with 1,6-Hexanediol. Diacetoxydimethylsilane (56.4 g, i.e., 0.32 mole) was added to a solution of 41.4 g (0.35 mole) of 1,6-hexanediol in 100 ml of dry chloroform. After the period of stirring, solvent was distilled off and the residue was vacuum-fractionated. The yield of 2,2-dimethyl-1,3-dioxa-2-silacyclononane, b.p. 140-142° (14 mm), was 26.1 g (47%); after redistillation it had the constants given in the table.

Reaction of Tetraacetoxysilane with 1,3-Butanediol. 1,3-Butanediol (35.1 g, i.e. 0.39 mole) was added to a solution of 50.2 g (0.19 mole) of tetraacetoxysilane in 50 ml of dry ether. Ether was distilled off, and the residue was vacuum-fractionated. After the theoretical amount of acetic acid had come over, a solid polymer remained in the distillation flask. Destructive vacuum distillation of this from a metal bath (bath temperature 200°) gave 33.0 g (85%) of Substance No.7, b.p. 120-122° (15 mm). After redistillation it had the contants given in the table. The literature [6] gives b.p. 115° (11.5 mm).

Reactions of Tetraacetoxysilane with 1,4-Butanediol and 1,5-Pentanediol. Reaction of tetraacetoxysilane under completely analogous conditions with 1,4-butanediol and with 1,5-pentanediol resulted only in the isolation of the diacetic esters of the glycols: $CH_3OCO(CH_2)_4OCOCH_3$; b.p. 110-111° (12 mm); d^{20}_4 1.0360; $n^{20}D$ 1.4300; ester value, found 650.3, 648.6, calculated 644.1 (yield 26%); $CH_3OCO(CH_2)_5OCOCH_3$; b.p. 134-135° (12 mm); d^{20}_4 1.0198; $n^{20}D$ 1.4831; ester value, found 581.9, calculated 596.1 (yield 16%).

SUMMARY

1. A new method was developed for the synthesis of 2,2-dialkyl-1,3-dioxa-2-silacycloalkanes by reaction between diacetoxydialkylsilanes and β-, γ-, δ-, and ϵ-glycols. By this method we synthesized four such compounds having 6-, 7-, 8-, and 9-membered rings; three of them were prepared for the first time.

2. Reaction of diacetoxydialkylsilanes with ethylene glycol and with 1,2-propanediol results in the formation of 2,2,7,7-tetraalkyl-1,3,6,8-tetroxa- 2,7- disilacyclodecanes and dimethyl derivatives of these, respectively-ly.

3. Reaction between tetraacetoxysilane and 1,3-butanediol gave 2,8-dimethyl-1,5,7,11-tetroxa-6-silaspiro-[5.5]undecane.

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SOME PROPERTIES OF Si-C$_{aryl}$ BONDS IN ORGANOSILICON COMPOUNDS CONTAINING A CARBONYL OR ESTER GROUP IN THE γ-POSITION

D. N. Andreev and E. V. Kukharskaia

In their study of the properties of 3-(trimethylsilyl)propionic acid, which was the first organosilicon acid of this type (containing a carboxy group in the γ-position with respect to silicon) to be prepared, Sommer and co-workers found that treatment of this compound with concentrated sulfuric acid resulted in the elimination of a methyl group as methane with formation of a compound which was hydrolyzed by water to give a high yield of a dicarboxylic acid containing a siloxane linkage [1]. Sommer and co-workers showed later [2] that the intermediate product was an organosilicon sulfuric ester, which was decomposed by water with formation of an Si-O-Si linkage.

$$(CH_3)_3SiCH_2CH_2COOH \xrightarrow{H_2SO_4} \underset{\overset{|}{CH_3}}{\overset{\overset{CH_3}{|}}{HOSO_3SiCH_2CH_2COOH}} + CH_4$$

$$\downarrow H_2O$$

$$[HOOCCH_2CH_2Si(CH_3)_2]_2O$$
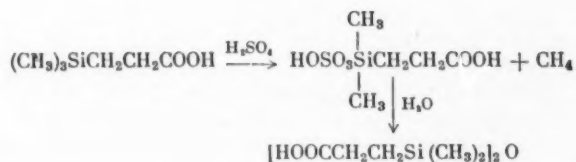
This interesting reaction was studied recently by Dolgov and ourselves [3] for the case of 3-(diethylmethylsilyl)propionic acid, and it was shown that in this case treatment with sulfuric acid again resulted in the elimination of a methyl group:

$$2CH_3(C_2H_5)_2SiCH_2CH_2COOH \xrightarrow[H_2O]{H_2SO_4} [HOOCCH_2CH_2Si(C_2H_5)_2]_2O + 2CH_4.$$
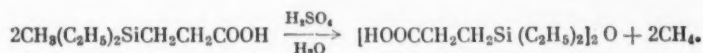
Another possible way of synthesizing dibasic organosilicon acids containing a siloxane linkage might be provided by the cleavage of the Si-C$_{aryl}$ bond in (alkylarylsilyl)propionic acids by means of dilute acids. We examined this possibility in the case of the synthesis of 4,6-diethyl-4,6-dimethyl-5-oxa-4,6-disilanonanedioic acid (III):

$$CH_3(C_2H_5)C_6H_5SiCH_2Cl + NaCH(COOC_2H_5)_2 \rightarrow CH_3(C_2H_5)C_6H_5SiCH_2CH(COOC_2H_5)_2$$
$$\text{(I)} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(II)}$$

$$\text{(II)} \xrightarrow{KOH}_{HCl} CH_3(C_2H_5)C_6H_5SiCH_2CH_2COOH \xrightarrow{HCl}_{H_2O} [HOOCCH_2CH_2Si(C_2H_5)CH_3]_2O + C_6H_6$$
$$\text{(III)}$$
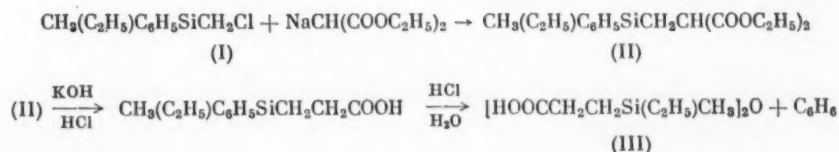
However, we did not succeed in isolating the intermediate monobasic organosilicon acid, 3-(ethylmethylphenylsilyl)propionic acid. When the product of the hydrolysis of (II) was neutralized with excess of hydrochloric acid, hydrolytic scission of the Si-C$_{aryl}$ bond occurred and the dibasic organosilicon acid (III) was obtained in 58% yield on the amount of the malonic ester taken. It should be noted that when Sommer's method was used the yield of dibasic acids had the similar value of 60-62%. As was to be expected, as a result of the unsymmetrical structure (presence of one methyl and one ethyl group on each silicon atom) of the acid (III), this compound was a liquid, and not a solid like its analogs, which contained only methyl or ethyl groups.

It was of interest to investigate how a malonic ester having two phenyl groups on the silicon atom would behave under the same conditions. It might be supposed that its hydrolysis would give a polysiloxane containing

$$-\underset{\underset{\displaystyle CH\ CH_2COOH}{|}}{\overset{\displaystyle R}{\overset{|}{Si}}} - O-.$$
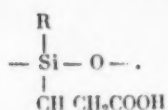
units in its chain. With this object we prepared the malonic ester (IV) by the action of sodio-malonic ester on (chloromethyl)methyldiphenylsilane, and this substance, unlike the malonic ester (II), was found to be very stable to hydrolytic scission and gave the substituted malonic acid (V) on hydrolysis. When heated to 140-150°, (V) was decarboxylated into 3-(methyldiphenylsilyl)propionic acid (VI). Heating of (VI) at 200-210° in a vacuum resulted, unexpectedly, in the elimination of a phenyl group with formation of the organosilicon ester (VI¹) in about 50% yield:

$$CH_3(C_6H_5)_2SiCH_2Cl + NaCH(COOC_2H_5)_2 \rightarrow CH_3(C_6H_5)_2SiCH_2CH(COOC_2H_5)_2$$
$$(IV)\ (35,7\%)$$

$$(IV) \xrightarrow[HCl]{KOH} CH_3(C_6H_5)_2SiCH_2CH(COOH)_2 \xrightarrow{140-150°} CH_3(C_6H_5)_2SiCH_2CH_2COOH$$
$$(V)\ (75.3\%) \hspace{3cm} (VI)\ (quantitative\ yield)$$

$$(VI) \xrightarrow[(6\ mm)]{200-210°} \underset{\underset{\displaystyle OOCCH_2CH_2Si(C_6H_5)_2CH_3}{|}}{\overset{\overset{\displaystyle |}{}}{CH_3(C_6H_5)SiCH_2CH_2COOH}}$$
$$(VII)\ (\sim50\%)$$
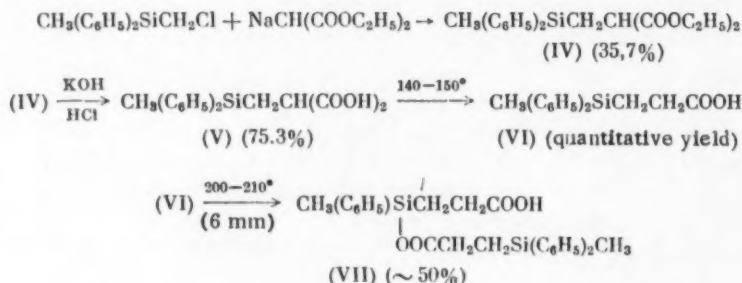
Hydrolysis of the ester gave the acid (VI), which confirms the structure of (VII).

It is known that Si-C_{aryl} is a bond of high thermal stability; sila hydrocarbons containing aryl groups can generally stand heating to 300° and over without decomposition. The observed elimination of a phenyl group at relatively low temperatures (200-210°) with formation of the ester (VII) must be ascribed to the presence in (VI) of a carboxy group, which at this temperature has been found to be capable of splitting the Si-C_{aryl} bond in a way which is to be compared with the action of dry hydrogen chloride in acetic acid solution [4].

$$\underset{\underset{\underset{\displaystyle [H\ \ ]OOCCH_2CH_2Si(C_6H_5)_2CH_3}{|}}{[C_6H_5]}}{\overset{\overset{\displaystyle C_6H_5}{|}}{CH_3-SiCH_2CH_2COOH}} \longrightarrow \underset{\underset{\displaystyle OOCCH_2CH_2Si(C_6H_5)_2CH_3}{|}}{\overset{\overset{\displaystyle C_6H_5}{|}}{CH_3SiCH_2CH_2COOH}} + C_6H_6$$
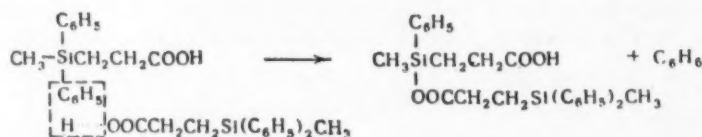
The difference in the stabilities of the malonic esters (II) and (IV) toward hydrolytic cleavage indicates that the presence of two phenyl groups on a silicon atom considerably raises the chemical stability of the Si-C_{aryl} to heterolytic (ionic) breakdown. On the other hand, the presence of the same two phenyl groups in the monobasic acid (VI) not only does not hinder, but possibly even helps the thermal breakdown of the Si-C_{aryl} of (VI) (or, more accurately, the thermal interaction of this bond with the hydrogen of the carboxy group of a second molecule of the same acid), resulting in the formation of an organosilicon ester of the organosilicon acid and of benzene.

EXPERIMENTAL

(Chloromethyl)ethylmethylphenylsilane (I). The starting compound for the synthesis of (I) was chloro(chloromethyl)methylphenylsilane, which was prepared by the action of phenylmagnesium bromide on dichloro(chloromethyl)methylsilane and had the following constants: b.p. 238-240°; $n^{20}D$ 1.5370; d^{20}_4 1.1986; found MR 53.35; calculated MR 54.57. The literature [5] gave b.p. 136° (24 mm).

A Grignard reagent was prepared from 36.5 g of magnesium (1.5 moles), 162.5 g of ethyl bromide, and 300 ml of dry ether, and to this we added 189 g (0.9 mole) of chloro(chloromethyl)methylphenylsilane. The mixture was heated for eight hours and then decomposed with dilute hydrochloric acid. The ether layer was separated, washed, and dried with calcium chloride. Ether was distilled off, and the residue was fractionated. The yield of (I) was 106 g (58%); b.p. 239-240°; $n^{20}D$ 1.5228; d^{20}_4 1.0179; found MR 59.61; calculated MR 59.57. Found Si 13.87; 14.21%; calculated for $C_{10}H_{15}ClSi$ 14.12%.

Diethyl [(Ethylmethylphenylsilyl)methyl]malonate (II).   Sodiomalonic ester was prepared from 20.7 g (0.90 mole) of sodium, 152.2 g (0.95 mole) of malonic ester, and 600 ml of absolute ethanol, and 180 g (0.90 mole) of (I) was added. The mixture was heated for 28 hours, alcohol was distilled off, and 200 ml of water and 100 ml of ether were added to the residue. The ether solution was separated, washed with water, and dried with anhydrous copper sulfate. Fractionation gave 166 g (57%) of (II); b.p. 201.5° (9 mm); $n^{20}D$ 1.4918; d^{20}_4 1.0369; found MR 90.17; calculated MR 90.68; found Si 8.70; 8.72%; calculated for $C_{17}H_{26}O_4Si$-8.70%.

4,6-Diethyl-4,6-dimethyl-5-oxa-4,6-disilanonanedioic Acid (III).   A solution of potassium hydroxide (112 g in 112 ml of water) was heated to 90° in a flask fitted with reflux condenser, and 163 g (0.5 mole) of (II) was added. The mixture was heated for 90 minutes and was then transferred to a porcelain dish and evaporated almost to dryness. The salt was disssolved in 200 ml of water, 200 ml of concentrated hydrochloric acid was added, the organic layer was separated, the aqueous layer was treated with ether, and the ether extract was combined with the organic layer. The solution was washed with water and dried with anhydrous copper sulfate; ether was distilled off, and the residue was fractionated. The yield of (III) was 44.7 g (58.4%); b.p. 254°; $n^{20}D$ 1.4633; d^{20}_4 1.0626; found MR 79.46; calculated MR 79.70; acid value: found 367, calculated 366; found Si 18.24; 18.32%; calculated for $C_{12}H_{26}O_5Si_2$-18.31%.

Diethyl [(methyldiphenylsilyl)methyl]malonate (IV).   Sodiomalonic ester was prepared from 23.2 g (1.01 moles) of sodium, 169.7 g (1.06 moles) of malonic ester, and 900 ml of absolute ethanol, and 200.0 g (1.01 moles) of (chloromethyl)methyldiphenylsilane ([6]; b.p. 169-170° (4 mm); $n^{20}D$ 1.5815; d^{20}_4 1.1077; found MR 74.31; calculated MR 74.76) was added. The mixture was heated for 28 hours. The further treatment was as in the preparation of (II). The yield of (IV) was 133.5 g (35.7%); b.p. 236-238° (6 mm); $n^{20}D$ 1.5366; d^{20}_4 1.0921; found MR 105.88; calculated MR 105.87; found Si 7.49; 7.39 %; calculated for $C_{21}H_{26}O_4Si$-7.57%.

[(Methyldiphenylsilyl)methyl]malonic Acid (V).   A solution of potassium hydroxide (76 g in 76 ml of water) was heated to 90° in a flask fitted with reflux condenser, and 129 g (0.35 mole) of (IV) was added. The mixture was heated for two hours and was then transferred to a porcelain dish and evaporated almost to dryness. The salt was dissolved in 200 ml of water, and 178 ml of concentrated hydrochloric acid was added. The further treatment was as in the preparation of (III). After removal of ether a crystalline product remained. It was crystallized from benzene, and the crystals were washed on the filter with hexane. The yield of (V) was 82.8 g (75.3%); m.p. 136°; acid value: found 359, 362, calculated 356; found Si 8.87; 8.69%; calculated for $C_{17}H_{18}O_4Si$-8.89%.

3-(Methyldiphenylsilyl)propionic Acid (VI).   The dicarboxylic acid (V) (6 g) was heated in a flask at 140-150° until the evolution of carbon dioxide ceased. The contents of the flask were crystallized from octane, and the crystals were washed on the filter with petroleum ether; the m.p. of (VI) was 59.5°; the yield was quantitative; acid number: found 211, 215; calculated 209; found Si 10.62; 10.45%; calculated for $C_{16}H_{18}O_2Si$-10.38%.

Organosilicon Ester of Organosilicon Acid (VII)*.   The dicarboxylic acid (V) (6 g) was decarboxylated at 140-150° until carbon dioxide ceased to be evolved, and the residue was then vacuum-distilled. The yield of (VII) was 2.5 g (about 50%); b.p. 236-240° (15 mm); $n^{20}D$ 1.5650; d^{20}_4 1.1282; found MR 133.56; calculated MR 134.09; hydrolysis value: found 240, 243, calculated 243; found Si 11.99; 11.94%, calculated for $C_{26}H_{30}O_4Si_2$-12.13%.

The ester (VII) is readily hydrolyzed, even by atmospheric moisture. By hydrolysis with water a crystalline substance was obtained; after two recrystallizations from octane it had m.p. 59°, undepressed by admixture of (VI).

SUMMARY

1. It was shown that organosilicon dibasic acids containing a siloxane linkage can be synthesized by the hydrolytic cleavage of an Si-C_{aryl} bond. In this way 4,6-diethyl-4,6-dimethyl-5-oxa-4,6-disilanonanedioic acid was synthesized.

2. The presence of two phenyl groups attached to silicon in a malonic ester greatly increases the stability of this compound to hydrolytic breakdown.

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* This ester may be called 4-methyl-6-oxo-4,9-diphenyl-5-oxa-4,9-disiladecanoic acid.

3. At 200°, 3-(methyldiphenylsilyl)propionic acid condenses with itself with elimination of benzene and the formation of an organosilicon ester of an organosilicon acid.

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[6] J. Speier, U. S. Patent 2527590; C. A. 45, 2968 (1951).

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* Original Russian pagination. See C. B. Translation.

ETHYLPHOSPHONOUS ESTERS AND SOME OF THEIR REACTIONS
COMMUNICATION 8. MIXED ANHYDRIDES OF DIALKYL PHOSPHITES, ALKYL ETHYLPHOSPHONITES AND DIETHYLPHOSPHINOUS ACIDS

B. A. Arbuzov, N. I. Rizpolozhenskii, and M. A. Zvereva

In 1951 Kosolapoff and Watson [1] prepared dipropyl- and dibutyl-phosphinic anhydrides for the first time by the action of dialkylphosphinic chlorides on dialkylphosphinic esters:

$$R_2P(O)Cl + ROP(O)R_2 \rightarrow R_2P - O - PR_2 + RCl,$$
$$\underset{O}{\|} \quad \underset{O}{\|}$$

in which

$$R = C_3H_7-; \; C_4H_9-.$$
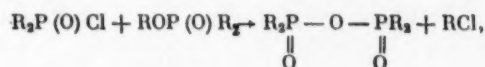
The same workers later obtained dimethyl- and diethyl-phosphinic anhydrides [2]. Kosolapoff did not succeed in preparing unsymmetrical dialkylphosphinic anhydrides [2,3]. No phosphinous anhydrides, which contain tervalent phosphorous, have been described in the literature.

In the present paper we describe the preparation of mixed anhydrides of diethylphosphinous acid and dialkyl phosphites and of ethyl ethylphosphonite and diethylphosphinous acid; some of their properties are reported. By the action of sodium dialkyl phosphite on chlorodiethylphosphine (diethylphosphinous chloride) we obtained mixed anhydrides of diethylphosphinous acid and dialkyl hydrogen phosphite in accordance with the scheme:

$$(C_2H_5)_2 PCl + NaOP(OR)_2 \rightarrow (C_2H_5)_2 P - O - P(OR)_2 + NaCl,$$

in which R = ethyl, propyl, or isopropyl.

We did not succeed in obtaining the dimethyl ester, because decomposition occurred during distillation. The products were liquids of unpleasant odor, extremely readily oxidized in the air. Cotton wool moistened with these substances immediately begins to smolder in the air. The constants of these compounds are given in Table 1.

The molecular refractions found for these anhydrides are less than those calculated for the structure indicated, by a constant amount (0.7).

The study of the chemical properties of this new type of organophosphorus compounds revealed some interesting peculiar features. Being tervalent phosphorus derivatives, the compounds combined vigorously with sulfur, though analysis showed that addition of only one atom of sulfur occurred. The addition of this sulfur atom may occur at either of the two phosphorus atoms, but it is more likely that it occurs at the phosphorus carrying two ethyl groups, because this phosphorus atom is closer in character to the phosphorus in a phosphine than the other:

$$(C_2H_5)_2 P - O - P(OC_2H_5)_2 + S \rightarrow (C_2H_5)_2 P - O - P(OC_2H_5)_2.$$
$$\underset{S}{\|}$$
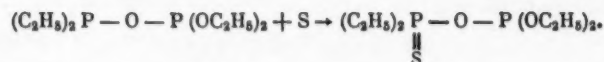
Indirect evidence of the correctness of the proposed structure of the product as a mixed anhydride of diethyl hydrogen phosphite and diethylphosphinothionic acid is provided by the formation of triethyl phosphite in the alcoholysis of the mixed anhydride with ethanol, which proves the absence of sulfur on the phosphorus carrying ethoxy groups. We did not succeed in isolating the other product of the alcoholysis (diethylphosphinothioic acid).

TABLE 1

No.	$(C_2H_5)_2P-O-P\,(OR)_2$	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated	Yield (%)
1	$(C_2H_5)_2P-O-P\,(OC_2H_5)_2$	90—92 (1)	1.4713	1.0407	61.13	61.75	60.5
2	$(C_2H_5)_2P-O-P\,(OC_3H_7-n)_2$	110—112 (2)	1.4702	1.0084	70.29	70.99	76.0
3	$(C_2H_5)_2P-O-P\,(OC_3H_7-i)_2$	90—91 (2)	1.4661	1.0006	70.32	70.99	71.0

• Values of AR: phosphorus in a phosphinic group 8.44; phosphorus in an ester group 7.04.

With the object of confirming the proposed structure for the sulfur-addition product, we carried out a confirmatory synthesis:

$$(C_2H_5)_2PCl + NaOP\,(CC_2H_5)_2 \rightarrow (C_2H_5)_2\,P-O-P\,(OC_2H_5)_2 + NaCl.$$
$$\overset{\parallel}{S} \qquad\qquad\qquad\qquad \overset{\parallel}{S}$$
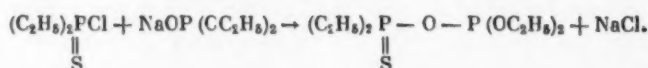
It will be seen from the comparative data in Table 2 that the two substances have almost identical constants.

We synthesized also the other isomer by the action of chlorodiethylphosphine on sodium diethyl phosphorothionate:

$$(C_2H_5)_2\,PCl + NaOP\,(OC_2H_5)_2 \rightarrow (C_2H_5)_2\,P-O-P\,(OC_2H_5)_2 + NaCl.$$
$$\overset{\parallel}{S} \qquad\qquad\qquad\qquad \overset{\parallel}{S}$$
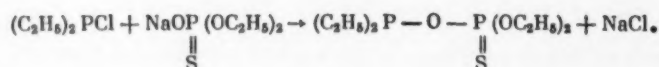
The constants of this product (No. 3, Table 2) differ considerably from those of No. 1 and No. 2, Table 2.

Unexpected results were obtained by the action of alkyl halides on mixed anhydrides of diethylphosphinic acid and dialkyl phosphites. On the assumption of the presence in the anhydride molecule of two tervalent phosphorus atoms, it would be expected that alkyl halides would add at both phosphorus atoms and that Arbuzov rearrangement could occur at the phosphorus carrying alkoxy groups. By the action of ethyl bromide (2 molecular proportions) on the mixed anhydride of diethylphosphinous acid and diethyl phosphite we obtained a crystalline product which was found to be tetraethylphosphonium bromide.

We made a more detailed study of the formation of phosphonium salts by the action of alkyl halides on the mixed anhydrides for the case of the mixed anhydride of diethylphosphinous acid and ethyl ethylphosphonite. This anhydride was prepared by the action of chlorodiethylphosphine on sodium ethyl ethylphosphonite:

$$(C_2H_5)_2PCl + NaOP\overset{\displaystyle OC_2H_5}{\underset{\displaystyle C_2H_5}{\diagup}} \rightarrow NaCl + (C_2H_5)_2P-O-P\overset{\displaystyle OC_2H_5}{\underset{\displaystyle C_2H_5}{\diagdown}}$$
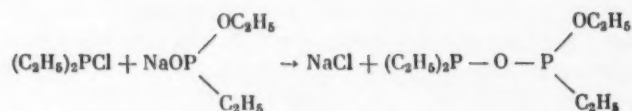
This mixed anhydride is a colorless liquid of unpleasant odor, which is spontaneously inflammable in the air. Its constants are: b.p. 91-93° (1.5 mm); d_4^{20} 1.0042; $n^{20}D$ 1.4868; calculated MR 60.81; found MR 6015.

The anhydride combined with only one atom of sulfur with formation of a product of b.p. 127-130° (1.5 mm). The reaction of the anhydride with alkyl halides was analogous with that described above for the mixed anhydride of diethylphosphinous acid and diethyl phosphite. In diethylphosphinous acid and ethyl ethylphosphonite we isolated tetraethylphosphonium bromide.

TABLE 2

No.	Method of preparation	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated
	$(C_2H_5)_2P-O-P(OC_2H_5)_2$ $\parallel$ S					
1	Anhydride prepared by the addition of sulfur	116—118(0.5)	1.5030	1.1182	68.32	67.79
2	Anhydride prepared from diethylphosphinothionic chloride	115—117(0.5)	1.5045	1.1190	68.33	67.79
	$(C_2H_5)_2P-O-P(OC_2H_5)_2$ $\parallel$ S					
3	Anhydride prepared from chlorodiethylphosphine and sodium diethyl phosphorothionate	111—113(0.5)	1.4870	1.1294	65.84	66.39

In order to determine the source of two of the ethyl groups of the tetraethylphosphonium bromide (from ethyl bromide or by transfer from the ethoxy group) we carried out experiments on the action of butyl and benzyl bromides on the mixed anhydride. In the first case we obtained dibutyldiethylphosphonium bromide, and in the second dibenzyldiethylphosphonium bromide. It was thus shown that two of the alkyl groups in the phosphonium salts obtained are derived from the alkyl halide used in the reaction.

This unexpected formation of tetraalkylphosphonium salts in the reaction of alkyl halides with mixed anhydrides may be explained as follows:

$$(C_2H_5)_2P-O-P(OC_2H_5)_2 + RBr \longrightarrow \left[(C_2H_5)_2\overset{+}{P}O-P(OC_2H_5)_2\right]\bar{B}r \longrightarrow (C_2H_5)_2PR + O=P(OC_2H_5)_2$$
$$\overset{R}{} \qquad \overset{Br}{}$$

$$(C_2H_5)_2P-R + RBr \longrightarrow \left[(C_2H_5)_2\overset{+}{P}\overset{R}{\underset{R}{<}}\right]\bar{B}r$$

$$(C_2H_5)_2P-O-P\overset{OC_2H_5}{\underset{C_2H_5}{<}} + RBr \longrightarrow \left[(C_2H_5)_2\overset{+}{P}-O-P\overset{OC_2H_5}{\underset{C_2H_5}{<}}\right]\bar{B}r \longrightarrow$$

$$(C_2H_5)_2PR + O=P\overset{OC_2H_5}{\underset{C_2H_5}{<}} + RBr \longrightarrow \left[(C_2H_5)_2\overset{+}{P}\overset{R}{\underset{R}{<}}\right]Br$$
$$\overset{Br}{}$$
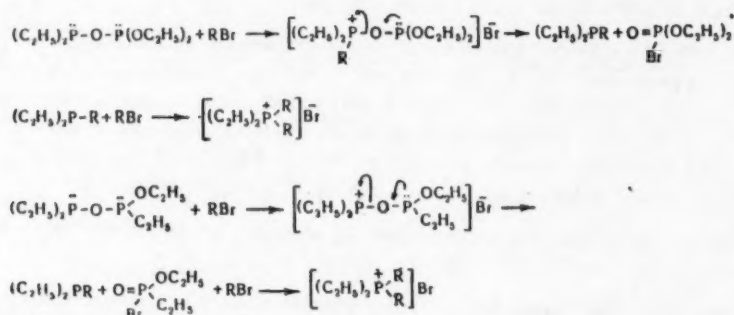
Alkyl halide first adds to the tervalent phosphorus atom most close in character to the phosphorus atom of a phosphine. As a result of electron transfer in the direction indicated by the arrows, cleavage of a P-O bond occurs with formation of a tertiary phosphine, which gives a quaternary phosphonium salt with the alkyl halide.

The other reaction product must be an acid bromide: in the first case, diethyl phosphorobromidate, and in the second case, ethyl ethylphosphonobromidate. We did not succeed in isolating these acid bromides, evidently because of their instability.

EXPERIMENTAL

Synthesis of Mixed Anhydrides of Dialkyl Hydrogen Phosphites and Diethylphosphinous Acid

Attempt to Synthesize the Mixed Anhydride of Dimethyl Hydrogen Phosphite and Diethylphosphinous Acid. A mixture of 14.5 g of dimethyl hydrogen phosphite, 15 g (1.8 g excess) of triethylamine, and 150 ml of dry ether was prepared in a four-necked flask fitted with reflux condenser, dropping funnel, stirrer, and tube for the passage of carbon dioxide. The flask was cooled externally with snow and salt, and a feeble stream of carbon dioxide was

passed while 16.3 g of chlorodiethylphosphine was added from the dropping funnel. When the whole of the calculated amount of chlorodiethylphosphine had been added, the mixture was stirred further at room temperature for two hours. Triethylamine hydrochloride was filtered off at the pump in a stream of carbon dioxide.

The weight of triethylamine hydrochloride was 17 g (94%). Ether was distilled off and left a pale-yellow mobile liquid having an unpleasant phosphine odor; it was vacuum-distilled from an Arbuzov flask. In distillation at a bath temperature of 130° about 1 g of a substance of wide boiling range (35-60° at 10 mm) came over; the substance being distilled decomposed with the separation of an orange precipitate.

Synthesis of the Mixed Anhydride of Diethyl Hydrogen Phosphite and Diethylphosphinous Acid. Sodium diethyl phosphite was prepared from 15.8 g of diethyl hydrogen phosphite and 3.6 g (1 g excess) of sodium in 150 ml of ether in the apparatus described above. The excess of sodium was removed. Chlorodiethylphosphine (14.3 g) was added with stirring. The reaction was carried out without cooling, and gentle reflux of ether occurred; the mixture was then heated in a water bath for two hours. Sodium chloride was filtered off at the pump in a stream of carbon dioxide.

Ether was removed under pressure, and the residue, a pale-yellow mobile liquid of unpleasant odor, was vacuum-distilled from an Arbuzov flask. The mixed anhydride (15.6 g) had b.p. 90-92° (1 mm); $n^{20}D$ 1.4713 d^{20}_4 1.0407; found MR 61.13; calculated for $C_8H_{20}P_2O_3$ MR 61.75; found %: P 27.42; 27.25; calculated %: P 27.44. It was an unpleasant-smelling, colorless liquid, readily oxidized by atmospheric oxygen. Cotton wool moistened with the anhydride began to smoke and smolder when exposed to the air.

Synthesis of the Mixed Anhydride of Dipropyl Hydrogen Phosphite and Diethylphosphinous Acid. The synthesis was in all ways analogous to that just described. The substances taken in the reaction were dipropyl hydrogen phosphite (19.6 g), sodium (4.3 g, an excess), ether (150 ml), and chlorodiethylphosphine (16.3 g). Sodium chloride was centrifuged off. The residue remaining (27.0 g) after removal of ether under reduced pressure was vacuum-fractionated. The mixed anhydride, which amounted to 19.5 g (76%), had b.p. 110-112° (2 mm); d^{20}_4 1.0084; $n^{20}D$ 1.4702; calculated for $C_{10}H_{24}P_2O_3$ MR 70.99; found MR 70.29; found %: P 24.32; 24.25; calculated %: P 24.4. It was an unpleasantly smelling colorless liquid which readily oxidized.

Synthesis of the Mixed Anhydride of Diisopropyl Hydrogen Phosphite and Diethylphosphinous Acid. Sodium diisopropyl phosphite was prepared from 14.4 g of diisopropyl hydrogen phosphite and 3.8 g (an excess) of sodium in 150 ml of ether, and 10.4 g of chlorodiethylphosphine was added. Sodium chloride was centrifuged off. The residue remaining (17.5 g) after removal of ether under reduced pressure, a yellowish mobile liquid, was vacuum-fractionated. The mixed anhydride, amounting to 11.6 g (71%), had b.p. 90-91° (2 mm); d^{20}_4 1.0006; $n^{20}D$ 1.4661; found MR 70.32; calculated for $C_{10}H_{24}P_2O_3$ MR 70.99; found %: P 24.56; 24.38; calculated %: P 24.4.

Like the other mixed anhydrides, it was a colorless liquid having an unpleasant phosphine odor; it was readily oxidized.

Action of Sulfur on the Mixed Anhydride of Diethyl Phosphite and Diethylphosphinous Acid. A three-necked 25-ml flask fitted with thermometer, reflux condenser, and tube for the passage of carbon dioxide was charged with 9.7 g (0.0428 mole) of the mixed anhydride, and 1.4 g (0.0428 mole) of sulfur powder was added; the temperature in the flask rose to 85°, but not all of the sulfur taken reacted. All the sulfur reacted when the mixture was heated to 150°. A further 1.4 g (0.0428 mole) of sulfur was then added, but this portion did not react in spite of heating for two hours at 150-160°. The unchanged sulfur was filtered off. Vacuum fractionation gave 4.8 g (43.5%) of the mixed anhydride of diethyl phosphite and diethylphosphinothionic acid; b.p. 116-118° (0.5 mm); d^{20}_4 1.1182; $n^{20}D$ 1.5030; found MR 68.32; calculated for $C_8H_{20}P_2O_3S$-MR 68.79; found %: P 23.78; 23.84; S 12.65; 12.72; calculated % P 24.03; S 12.4.

Synthesis of the Mixed Anhydride of Diethyl Phosphite and Diethylphosphinothionic Acid. Sodium diethyl phosphite was prepared in a three-necked flask from 14.3 g of diethyl phosphite and 3.5 g of sodium (an excess) in 200 ml of gasoline (b.p. 40-80°). To this solution 16.2 g of diethylphosphinothionic chloride was added. No cooling was applied during mixing and the mixture was then refluxed for two hours. Sodium chloride was removed by centrifuging and gasoline was distilled off under reduced pressure. Fractional distillation gave 13.2 g (55.7%) of the mixed anhydride of diethyl phosphite and diethylphosphinothionic acid; b.p. 115-117° (0.5 mm); d^{20}_4 1.1190; $n^{20}D$ 1.5045; found MR 68.33 calculated for $C_8H_{20}P_2O_3S$ MR 67.79; found %: P 23.68; 23.75; S 12.84; 12.73; calculated %: P 24.03; S 12.4.

Synthesis of the Mixed Anhydride of Diethyl Phosphorothionate and Diethylphosphinous Acid. Sodium diethylphosphite was prepared in a three-necked flask from 20.7 g of diethyl phosphite and 4.5 g (an excess) of sodium in 200 ml of gasoline (b.p. 40-80°). By the addition of 4.7 g of sulfur powder the product was converted into sodium diethyl phosphorothionate. To the solution of this salt 18.7 g of chlorodiethylphosphine was added. No cooling was applied during mixing, and the mixture was then refluxed for two hours. Sodium chloride was removed by centrifuging. The residue remaining after the removal of gasoline under reduced pressure was fractionated. The mixed anhydride (6 g) had b.p. 111-113° (0.5 mm); d^{20}_4 1.1294; $n^{20}D$ 1.4870; found MR 65.84; calculated for $C_8H_{20}P_2O_3S$ MR 66.39; found %: P 23.85; 23.71; S 12.82; 12.76; calculated %: P 24.03; S 12.4.

Alcoholysis of the Mixed Anhydride of Diethyl Phosphite and Diethylphosphinothionic Acid. A mixture of 40 ml of absolute ethanol, 0.1 g of sodium, and 10 ml of the mixed anhydride (prepared by the addition of sulfur to the mixed anhydride of diethyl phosphite and diethylphosphinous acid) was prepared in a flask fitted with reflux condenser. The mixture was refluxed for six hours. Alcohol was distilled off, and the residue was vacuum-fractionated. According to its analysis and constants, Fraction I was triethyl phosphite; b.p. 50-52° (14 mm); d^{20}_4 0.9680; $n^{20}D$ 1.4128; found%: P 19.38; 18.44; calculated for $C_6H_{15}PO$%: 18.67. Fraction II had an extended boiling range (52-125°). No chemically pure substance could be isolated.

Action of Ethyl Bromide on the Mixed Anhydride of Diethyl Phosphite and Diethylphosphinous Acid. A mixture of 9.5 g of the mixed anhydride and 9.3 g of ethyl bromide was sealed in a glass tube. The tube was heated in oil. At an oil temperature of 100° crystals began to form, and these quickly filled almost the whole of the volume previously occupied by liquid. A large amount of decomposition products ("yellow phosphorus") appeared at the bottom of the tube. Heating of the tube was continued for two hours at 100-110° (temperature of oil). When the tube was opened there was no evidence of any excess pressure; after crystallization the crystals melted with decomposition at 317-319°. Found %: P 13.85; 13.74; Br 34.98; 35.12; calculated for C_8H_{20} PBr %: P 13.65; Br 35.30.

The analysis and melting point confirm that the substance was tetraethylphosphonium bromide.

Synthesis of the Mixed Anhydride of Diethylphosphinous Acid and Ethyl Ethylphosphonite

Sodium ethyl ethylphosphonite was prepared from 3.3 g (an excess) of sodium and 15.0 g of ethyl hydrogen ethylphosphonite in 150 ml of ether in a four-necked flask fitted with reflux condenser, dropping funnel, stirrer, and tube for the passage of carbon dioxide. The mixture was stirred and cooled with snow and salt while 15.3 g of chlorodiethylphosphine was added. The mixture was then refluxed for two hours. Sodium chloride was filtered off at the pump. Ether was removed under reduced pressure, and the residue was fractionated. The mixed anhydride amounted to 15.7 g (61.5%) and had b.p. 91-93° (1.5 mm); d^{20}_4 1.0042; $n^{20}D$ 1.4868; found MR 60.15, calculated for $C_8H_{20}P_2O_2$ MR 60.81; found %: P 29.46; 29.38; calculated %: P 29.55.

It was a colorless liquid with a very unpleasant phosphine odor; it was spontaneously inflammable in air, and all operations in its preparation were therefore carried out in an atmosphere of carbon dioxide.

Action of Ethyl Bromide on the Mixed Anhydride of Diethylphosphinous Acid and Ethyl Ethylphosphonite. A mixture of 3.4 g of the mixed anhydride and 1.8 g of ethyl bromide was prepared in a three-necked flask fitted with reflux condenser, thermometer, and tube for the passage of carbon dioxide. There was no reaction in the cold. The mixture was heated, and when the temperature in the flask reached 80° a very vigorous reaction began. Heating was stopped, but the temperature in the flask rose rapidly and attained 195°. On cooling, the contents of the flask solidified. Recrystallization from a mixture of isopropyl alcohol and 2-butanone gave needles of m.p. 317-319° (with decomposition). Found %: P 13.45; 13.53; Br 34.92; 34.83; C 42.08; H 8.68; calculated for $C_8H_{20}PBr$%: P 13.65; Br 35.3; C 42.3; H 8.8. The analysis and melting point confirm that the substance was tetraethylphosphonium bromide.

Action of Butyl Bromide on the Mixed Anhydride of Diethylphosphinous Acid and Ethyl Ethylphosphonite. The procedure was as described above. The reactants were the mixed anhydride (2.5 g) and butyl bromide (3.5 g); there was no reaction in the cold. When the mixture was heated to 100° reaction began. Heating was stopped. The temperature in the flask rose rapidly and reached 165° toward the end of the reaction. On cooling, the contents of the flask solidified. Recrystallization from a mixture of 2-butanone and isopropyl alcohol gave needles of m.p. 146-148°. Found %: P 11.15; 11.22; Br 27.92; 28.17; C 50.61; H 9.75; calculated for $C_{12}H_{28}PBr$%: P 10.98; Br 28.28; C 50.89; H 9.93.

The analysis confirms that in this case dibutyldiethylphosphonium bromide was obtained.

Action of Benzyl Bromide on the Mixed Anhydride of Diethylphosphinous Acid and Ethyl Ethylphosphonite.
The substances taken for reaction were the mixed anhydride (2.0 g) and benzyl bromide (3.3 g). The benzyl
bromide was added in portions. When the first portion (about one-third of the whole) was added, the temperature
in the flask rose from 20° to 125°; the mixture was cooled to 80° and the second portion was added, when the
temperature in the flask rose to 150°. The mixture was heated in an oil bath at 160-165° for two hours. When
cool, the mixture formed a yellowish, glassy mass, which crystallized after two weeks. Recrystallization from
2-butanone gave needles of m.p. 234-238° (with decomposition). Found %: P 8.95; 8.78; Br 22.55; 22.71; cal-
culated for $C_{18}H_{24}P\ Br$ %: P 8.83; Br 22.8. The product was dibenzyldiethylphosphonium bromide.

SUMMARY

1. Mixed anhydrides of the following types were prepared: $(Et)_2\ P - O - P\ (OR)_2$

$$(R = C_2H_5;\ C_3H_7\text{-}n;\ C_3H_7\text{-}i)\quad (C_2H_5)_2\ P - O - P \begin{cases} OC_2H_5 \\ C_2H_5 \end{cases}$$
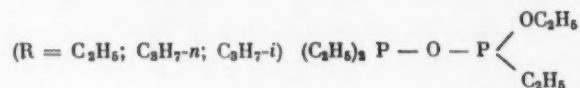
2. When mixed anhydrides of these types are treated with alkyl halides, tetraalkylphosphonium halides are
formed.

3. In the reaction of the mixed anhydrides with sulfur, only one sulfur atom is taken up, and this adds at
the phosphorus atom carrying two ethyl groups.

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CATALYTIC SYNTHESIS OF NITRILES

COMMUNICATION 1. "NITRILATION" OF BUTYL ALCOHOL

WITH AMMONIA IN PRESENCE OF NICKEL-ALUMINA CATALYSTS

M. A. Popov and N. I. Shuikin

Several investigations on the catalytic synthesis of nitriles have been reported. Thus, Mailhe and de Godon [1] converted isopentylamine and other amines into the corresponding nitriles at 320-330° in presence of nickel. When copper was used for the same purpose, only partial conversion of isopentylamine into nitrile occurred. In a study of the amination of alcohols with ammonia, Brown and Reid [2] found that the highest yields of nitriles are obtained in presence of thoria deposited on asbestos. In experiments with this catalyst butyl alcohol and ammonia at 380-410° gave butyronitrile in only 11-22.3% yield. According to an American method [3] aliphatic nitriles may be obtained by passage of a mixture of an alcohol and ammonia over a silver or copper catalyst at 300-400°. In one of his patents, Teter [4] states that propionitrile can be prepared by subjecting a mixture of 1 mole of propene and 3-7 moles of ammonia to pressure at a high temperature in presence of a catalyst consisting of nickel or cobalt on a carrier.

Stearo- and palmito-nitriles can be prepared [5] by heating the acids in a stream of ammonia at 340-345°; a yield of 82% is obtained after seven hours and a yield of 90% after ten hours. Lauric acid was converted into the corresponding nitrile by this method when an addition was made of zinc chloride or phosphoric acid. Oleic and erucic acids were similarly converted into nitriles in 75-80% yield at 280-300°. In an investigation of the catalytic amination of C_4 alcohols one of us found [6] that with ammonia at 350° in presence of platinized charcoal isobutyl alcohol gave a 24.4% yield of isobutyronitrile, while n-butyl alcohol was partially converted into butyronitrile (28% yield) at 450° in presence of platinized silica gel. We must refer also to two papers by Plate and Vol'pin [7] concerning the reaction of olefins with ammonia in presence of an alimina-molybdia catalyst at 484°. They found that, regardless of the nature of the original olefin, the catalyzate contained acetonitrile in amounts of 16.7-41.6 moles per cent on the amount of olefin passed. The authors concluded that acetonitrile was formed as a result of dehydrogenation and subsequent breakdown of intermediately formed isopropylamine.

These examples show that amines, alcohols, acids, olefins, and ammonia have been used for the catalytic synthesis of nitriles. Reduced nickel, cobalt, copper, silver, and platinum, thorium and molybdenum oxides on carriers, and dehydrating substances, such as zinc chloride and phosphoric acid, have been used as catalysts. In our opinion, olefins and alcohols are the most accessible substances for use in the preparation of nitriles with the aid of ammonia. In view of the great practical importance of nitriles we have now carried out an investigation with the object of finding effective catalysts for the synthesis of nitriles from an alcohol or olefin and ammonia. We selected butyl alcohol and 1-hexene as reactants.

In view of the information in the literature, in our "nitrilation" experiments we used catalysts containing nickel, cobalt, molybdia, zinc chloride, cuprous chloride, and zinc and cobalt phosphates deposited on pumice, active charcoal, magnesia or active alumina. However, numerous experiments on the nitrilation of 1-hexene in presence of these catalysts at various temperatures showed that only very low yields (2.3-6.7%) of the corresponding nitrile could be obtained. Thus, in the passage of 1-hexene and ammonia taken in a molar ratio of 1 : 3 over a cobalt-nickel catalyst (on charcoal) at 300° at a space velocity of 0.2 hour $^{-1}$ we obtained hexanenitrile (b.p. 162° / 748 mm) in 3.8% yield; at 400° the yield was still only 6.7%.

We therefore gave our main attention to the nitrilation of alcohols, particularly butyl alcohol, in presence of nickel-alumina catalysts. We found conditions under which butyronitrile was obtained in 81.5% yield. We propose to extend this reaction to other aliphatic, alicyclic, and aromatic alcohols:

$$\text{Alk.CH}_2\text{OH} + \text{NH}_3 \xrightarrow{\text{Ni-Al}_2\text{O}_3} \text{Alk.CN} + 2\text{H}_2 + \text{H}_2\text{O}$$

$$\text{◇—CH}_2\text{OH} + \text{NH}_3 \xrightarrow{\text{Ni-Al}_2\text{O}_3} \text{◇—CN} + 2\text{H}_2 + \text{H}_2\text{O}$$

$$\text{⬡(H)—CH}_2\text{OH} + \text{NH}_3 \xrightarrow{\text{Ni-Al}_2\text{O}_3} \text{⬡(H)—CN} + 2\text{H}_2 + \text{H}_2\text{O}$$

$$\text{Ar. CH}_2\text{OH} + \text{NH}_3 \xrightarrow{\text{Ni-Al}_2\text{O}_3} \text{Ar. CN} + 2\text{H}_2 + \text{H}_2\text{O}$$
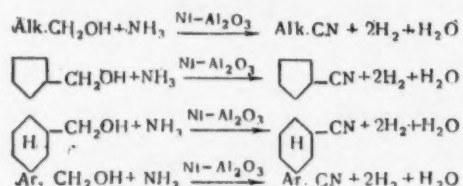
EXPERIMENTAL

For our nitrilation experiments we took commercial pure butyl alcohol; b.p. 117° (754 mm); d^{20}_4 0.8097; n^{20}D 1.3990. After exploratory experiments with various catalysts, consisting of reduced nickel and cobalt on various carriers (activated charcoal, pumice, MoO_2, MgO, and Al_2O_3), we decided to investigate in greater detail the activities and stabilities of a series of nickel-alumina catalysts (containing 30-1% of reduced nickel) in the reaction between ammonia and butyl alcohol; 100 ml of catalyst was placed in a catalysis tube in an electric furnace fitted with a thermoregulator. Butyl alcohol entered from an automatic buret at a space velocity of 0.2 hour^{-1}. Pure ammonia, in a 200% excess, entered the catalysis tube simultaneously. The liquid catalyzate was condensed in a receiver cooled in ice and salt. The gaseous reaction products were collected in a graduated gas holder over water, which absorbed the excess of ammonia. The nitrile content of the catalyzate was determined by hydrolyzing a sample with 50% sulfuric acid and subsequent distillation of the butyric acid into 0.5 N NaOH, which was then back-titrated with hydrochloric acid. Also, butyronitrile was isolated in the pure state by removal of amines and unchanged butyl alcohol from the nitrile part of the catalyzate and fractionation.

The experimental conditions and the results of the nitrilation of butyl alcohol are given in Table 1.

Experiments 1-7 were carried out with a catalyst containing 30% of nickel. The greatest amount of nitrile (82.5-84.9%) was obtained in the catalyzates from experiments at 300-330°. Raising or lowering the temperature resulted in considerable reduction in the nitrile content of the catalyzate. A temperature of 300° must be regarded as optimum for the nitrilation of butyl alcohol. Experiment 7, which lasted 18.5 hours, was carried out to determine the stability of the catalyst. Table 1 gives the results for the first, fifth, tenth, fifteenth, and nineteenth hours of work. In the course of this time 296 g of alcohol was consumed and 236.3 g of dry catalyzate was obtained (79.8% on the amount of alcohol taken). In the course of 18.5 hours of operation with the same catalyst, the nitrile content of the catalyzate fell by only 3.2%, i.e., from 79.5% to 76.3%.

Experiment 8, which last for five hours, was carried out at 300° with a catalyst containing 15% nickel. Table 1 gives the results for the first, third, and fifth hours of the work of the catalyst. In all, 80 g of alcohol was consumed and 62.4 g of dry catalyzate was obtained (78% on the amount of alcohol taken). The nitrile content of the catalyzate was 86.3-88.7%. Experiment 9 with a catalyst containing 7.5% of nickel was carried out under the same conditions. From 80 g of the alcohol we obtained 64 g (80%) of catalyzate containing 88.6-89.4% of nitrile. We then carried out Experiment 10 at 300° with a catalyst containing 3% of nickel and for a period of 15.5 hours. Table 1 gives the results for the first, third, fifth, tenth, and sixteenth hours of the work of the catalyst. In the course of this time 248 g of butyl alcohol was consumed and 223.2 g of dry catalyzate was formed (90.2% on the amount of butyl alcohol taken). The nitrile content of the catalyzate varied from 87.1% to 91.8%. Finally, Experiment 11 was carreid out with a catalyst containing only 1% of nickel. In the course of five hours 80 g of alcohol was consumed and 78.5 g of dry catalyzate was obtained (98.1% on the amount of butyl alcohol taken). The catalyzate obtained after the first hour contained 23.3% of nitrile, that obtained after the second hour 25.0%, and that obtained after the fifth hour 10.4%.

At 300° the amount of gaseous products was 8-15 liters; they consisted mainly of hydrogen (73-95%) with some 1-butene (3-6%), from which we prepared the dibromide, b.p. 166° (755 mm). Amines and unchanged alcohol were removed from the catalyzates. Amines were removed by extraction with dilute hydrochloric acid, treatment with sodium hydroxide solution, and fractional distillation. Separation of unchanged butyl alcohol from butyronitrile was effected by treatment of the amine-free dry catalyzate with concentrated sulfuric acid with careful cooling.

TABLE 1

Nitrilation of Butyl Alcohol with Ammonia over Nickel-Alumina Catalysts

Experiment	Catalyst	Temp.	Duration of exp. (minutes)	Amount (g) taken for reaction of		Amount of dry catalyzate	Amt. of gas (liters at STP)	Nitrile content of catalyzate (%)
				alcohol	ammonia			
1	30% Ni — Al$_2$O$_3$	240	30	8.0	4.4	7.0	1.9	27.5
2	Ditto	270	30	8.0	4.4	7.1	3.9	33.9
3	»	300	30	8.0	4.8	6.5	4.5	82.5
4	»	330	30	8.0	4.4	4.6	—	84.9
5	»	360	30	8.0	4.4	4.0	—	65.4
6	»	390	30	8.0	4.4	2.3	—	7.4
7—1	»	300	60	16.0	8.6	10.0	7.9	79.5
7—5	»	300	60	16.0	8.4	11.5	—	73.4
7—10	»	300	60	16.0	8.6	12.6	8.1	72.7
7—15	»	300	60	16.0	7.7	10.7	—	75.7
7—19	»	300	60	8.0	3.0	7.4	—	76.3
8—1	15% Ni — Al$_2$O$_3$	300	60	16.0	7.5	12.7	12.0	86.3
8—3	Ditto	300	60	16.0	8.6	12.5	—	88.7
8—5	»	300	60	16.0	8.8	12.7	—	86.8
9—1	7,5% Ni — A$_2$O$_3$	300	60	16.0	7.5	12.9	14.9	89.4
9—3	Ditto	300	60	16.0	7.5	12.8	—	89.3
9—5	»	300	60	16.0	8.6	12.8	—	88.6
10—1	3% Ni — Al$_2$O$_3$	300	60	16.0	8.8	13.5	12.7	87.1
10—3	Ditto	300	60	16.0	8.6	13.0	—	91.8
10—5	»	300	60	16.0	8.8	15.1	—	88.1
10—10	»	300	60	16.0	8.8	16.6	—	90.1
10—16	»	300	30	8.0	4.4	7.4	—	88.1
11—1	1% Ni — Al$_2$O$_3$	300	60	16.0	8.4	16.6	13.5	23.2
11—3	Ditto	300	60	6.0	8.2	16.1	—	25.0
11—5	»	300	60	16.0	8.8	16.4	—	10.4

Butyl hydrogen sulfate was then extracted with water, also under cooling. Butyl alcohol was recovered by treating the solution of butyl hydrogen sulfate with alkali, and heating; it was dried with potassium carbonate and distilled twice through a column. After being dried, the residual nitrile was fractionated. Part of it was hydrolyzed to butyric acid (b.p. 162° at 756 mm), from which we prepared the anilide, m.p. 96°.

From 64.0 g of the catalyzate from Experiment 7 we obtained 2.2 g of a mixture of amines and 5.2 g of butyl alcohol; b.p. 117° (755 mm), d^{20}_4 0.8098; n^{20}D 1.3992. Fractionation of the nitrile part at 745 mm gave:

> Fraction I, b.p. 90-114°; 1.2 g
> Fraction II, b.p. 114-116°; 51.5 g; d^{20}_4 0.7943; n^{20}D 1.3825
> Residue . . . . 0.5 g

According to the literature, butyl alcohol has b.p. 117.2° (760 mm) [8], d^{20}_4 0.8099, and n^{20}D 1.3991 [9], butyronitrile has b.p. 115.4-115.6° (739 mm) [10], d^{20}_4 0.7936 [11], and n^{24}D 1.3816 [11], and butyranilide has m.p. 96°.

Hence the alcohol isolated was unchanged butyl alcohol, and the nitrile was butyronitrile; the yield of this in Experiment 7 was 73.8% on the amount of alcohol that reacted.

From 35.5 g of the catalyzate from Experiment 8 we isolated 0.4 g of a mixture of amines and 2.0 g of butyl alcohol, b.p. 117° (748 mm); d^{20}_4 0.8098, and n^{20}D 1.3990.

Fractionation of the nitrile part of the catalyzate at 748 mm gave:

> Fraction I, b.p. 90-114°; 1.9 g
> Fraction II, b.p. 114-116°; 28.1 g; d^{20}_4 0.7941; n^{20}D 1.3823;
> the anilide of the acid had m.p. 96°
>
> Residue . . . . 0.6 g

The yield of butyronitrile was 69.2% on the amount of alcohol that reacted.

From 43.0 g of the catalyzate from Experiment 9 we obtained 0.4 g of a mixture of amines and 5.0 g of butyl alcohol, b.p. 117° (752 mm); d^{20}_4 0.8098; $n^{20}D$ 1.3989.

Fractionation of the nitrile part of the catalyzate at 752 mm gave:

Fraction I, b.p. 95-114°; 0.5 g
Fraction II, b.p. 114-116°; 32.6 g; d^{20}_4 0.7945; $n^{20}D$ 1.3824
Residue. . . . 1.5 g

The yield of nitrile was 71.7% on the amount of alcohol that reacted.

From 180.0 g of the catalyzate from Experiment 10 we isolated 2.0 g of a mixture of amines and 13.5 g of butyl alcohol, b.p. 117° (756 mm); d^{20}_4 0.8097, and $n^{20}D$ 1.3991.

Fractionation of the nitrile part of the catalyzate at 756 mm gave:

Fraction I, b.p. 103-114°; 2.1 g
Fraction II, b.p. 114-116°; 141.9 g; d^{20}_4 0.7935; $n^{20}D$ 1.3827
the anilide of the acid had m.p. 95.5°
Residue 13.7

The yield of nitrile was 81.5%.

From 70 g of the catalyzate from Experiment 11 we isolated 24.9 g of a mixture of amines of b.p. 70-160° 754 mm) and 9.4 g butyl alcohol, b.p. 116-117° (748 mm), d^{20}_4 0.8097, and $n^{20}D$ 1.3993. Fractionation of the nitrile part of the catalyzate at 748 mm gave:

Fraction I, b.p. 84-114°; 7.5 g
Fraction II, b.p. 114-116°, 14.6 g; d^{20}_4 0.7933; $n^{20}D$ 1.3832
Residue . . . . 8.0 g

The yield of butyronitrile was 32.8%.

The amines isolated from the condensates of Experiments 7-10 (5.0 g) were combined and distilled twice at 748 mm.

The following fractions were isolated:

Fraction I, b.p. 76-78°; 3.4 g; d^{20}_4 0.7399
Fraction II, b.p. 78-156°; 0.2 g
Fraction III, b.p. 156-158°; 0.8 g d^{20}_4 0.7664
Residue . . . . 0.3 g

For Fraction I: Found % N : 19.20; calculated for $C_4H_{11}N$ %N : 19.15. For Fraction III: Found % N : 10.73; calculated for $C_9H_{19}N$ %N 10.81. On the basis of its analysis and properties Fraction I consisted of butylamine and Fraction III of dibutylamine.

Hence the nitrilation of butyl alcohol in presence of catalysts having various contents of reduced nickel supported on active alumina proceeded very satisfactorily. The experiments showed that with catalysts having nickel contents raging from 3% to 30% catalyzates containing 72.7-91.8% of butyronitrile were obtained. The relation of the yield of nitrile to the nickel content of the catalyst is illustrated in Table 2.

It will be seen from Table 2 that a catalyst consisting of 3% of nickel on active alumina is the most effective in the nitrilation of butyl alcohol with ammonia. The optimum temperature for this reaction is 300°. Apart from nitrile, the condensates contain a small amount of mono- and di-butylamines. These amines are in themselves valuable, and their isolation from the catalyzates does not present particular difficulty. The amount of amines formed increases sharply when the nickel content of the catalyst is reduced to 1%.

TABLE 2

Yields of Butyronitrile obtained with Various Samples of Nickel Catalyst

Nickel content of catalyst (%)	Amount of nitrile isolated from condensate (%)
30	73,8
15	69,2
7,5	71,7
3	81,5
1	32,8

In the nitrilation of butyl alcohol some gaseous substances are also formed; the main component of these is hydrogen (73-95%), and there are small amounts of 1-butene (3-6%). In the experiments at 300°, one mole of butyl alcohol yielded 36.5-68.9 liters (STP) of gas, i.e.,52.7 liters on the average. The reaction of butyl alcohol with ammonia can be expressed by the equation:

$$CH_3CH_2CH_2CH_2OH + NH_3 = CH_3CH_2CH_2CN + H_2O + 2H_2,$$

which indicates that one mole of the alcohol should yield 44.8 liters of hydrogen. As a by-product a little 1-butene is formed as a result of the dehydration of the alcohol:

$$CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH=CH_2 + H_2O.$$
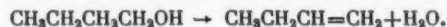
The experiments showed that the qualitative and quantitative compositions of the liquid and gaseous reaction products were in accord with the equation given. The amounts of by-products and unchanged alcohol were extremely small.

SUMMARY

1. An investigation was made of the "nitrilation" of butyl alcohol with ammonia in presence of various samples of nickel-alumina catalyst at 240-400° under atmospheric pressure.

2. The most effective catalyst for the nitrilation of butyl alcohol consisted of 3% of reduced nickel supported by active alumina. At 300° in presence of this catalyst the yield of butyronitrile was 81.5%.

3. Under similar conditions in presence of a cobalt-nickel (on active charcoal) catalyst 1-hexene gave only 3.8-6.7% of the corresponding nitrile.

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OXIDE-METAL CATALYSTS FOR THE REFORMING OF GASOLINES

COMMUNICATION 4. REFORMING OF THE 89.5-126°
FRACTION OF THE GASOLINE OF PETROLEUMS OF THE VOLGA-URALS GROUP
OVER A PALLADIUM CATALYST TREATED WITH HYDROGEN SULFIDE

Kh. M. Minachev, N. I. Shuikin, M. A. Riashentseva, and N. F. Kononov

In the preceding communication [1] we reported the results of a comparative investigation of two samples of palladium catalyst (0.5% Pd on Al_2O_3; differing in method of preparation) under the conditions of the reforming of the 89.5-126° fraction of petroleums of the Volga-Urals region (470-480°, hydrogen at 20 atm, space velocity of feed v 1.0 hour^{-1}, molar ratio of recirculating hydrogen to gasoline (H_2 : HC) 12.5 : 1). Analysis of the results showed that both samples of catalyst brought about not only the dehydrogenation of cyclohexanes, but also dehydroisomerization of cyclopentanes, skeletal isomerization of paraffins, and almost complete desulfurization of the gasoline. However, in spite of their high activities, particularly during the first five hours of work, with time both catalysts rapidly became less active, and after fifteen hours the aromatizing power of Catalyst No. 2 (which gave better results than Catalyst No. 1) had fallen by 40%. Such rapid fall in acitivity could be caused by partial poisoning of the catalysts by sulfur compounds (the sulfur content of the original gasoline was 0.017%.

It is possible that we shall succeed in replacing the scarce platinum catalysts for the reforming of gasoline by palladium catalysts, and the question of the stability of palladium catalysts is becoming very important; in the present investigation we attempted to prepare a stable palladium catalyst.

The first work in this direction was carried out recently by the present authors [2], who submitted a catalyst containing 0.5% of palladium on alumina to treatment with hydrogen sulfide with the object of making it stable under the conditions of the reforming of the 98-109° fraction of straight-run gasolines from Ilsk-Khadyzhin petroleums of low sulfur content (0.0025%). Our trials showed that this catalyst was very active and had quite satisfactory stability (260 hours of work without loss of activity). There is now a fair amount of material in the literature concerning the successful application of metal sulfides such as CoS and Ni_3S_2 [3-5] on various carriers for the purpose of the hydrodesulfurization, hydrogenation, and dehydrogenation of hydrocarbons. There are also references in patents [6] to the possibility of obtaining an active and stable platinum-alumina catalyst by treating it with hydrogen sulfide.

Although no satisfactory attempt has yet been made to explain the protective effect of hydrogen sulfide in raising the stabilities of catalysts containing Group VIII metals, the beneficial effect of such treatment is quite clear. It is possible that the experimental material now accumulating in this field will enable us to explain this undoubted relationship and to facilitate the development of stable palladium catalysts suitable for the reforming of sulfur-containing gasolines.

Our task in the present work was the investigation of the activity and stability of a "sulfurized" palladium catalyst under the conditions of the reforming of the 89.5-126° fraction of the gasoline of Volga-Urals petroleums and the comparison of the results with those of the preceding investigation [1]. Also, in order to determine the extent of the participation of the various classes of hydrocarbons in the reforming of this fraction, both the original fraction and the catalyzate were subjected to detailed analysis for the contents of individual hydrocarbons.

EXPERIMENTAL

Hydrated alumina was prepared by the precipitation of 1 M $Al(NO_3)_3$ with 12% aqueous ammonia. The resulting hydrogel was washed free from nitrate ions with distilled water, filtered, and dried for eight hours at 140° The dried mass was treated with dilute hydrofluoric acid (in an amount corresponding to 0.5% F on the weight of Al_2O_3) and then calcined at 500° for four hours. The mass was then ground to a powder, and pressed in a special press into cylindrical tablets 5 mm in diameter and in height. The cylinders were impregnated with H_2PdCl_4 solution of the necessary concentration, and were dried at 110-120°. The catalyst so obtained was treated with H_2S at 110° in a flow system for six hours (until moisture was completely removed from the catalyst).

Both the original fraction and the liquid catalyzate were analyzed for contents of aromatic hydrocarbons (sulfuric acid method) and sulfur (lamp method). The individual-hydrocarbon compositions of the original fraction and the catalyzates were determined by the combined method [7]. The gaseous catalysis products were analyzed in a VTI apparatus.

The 89.5-126° fraction of the gasoline of petroleums of the Volga-Urals group had n_D^{20} 1.4040 and d_4^{20} 0.7187; the content of aromatic hydrocarbons was 7.0% by volume, and the sulfur content was 0.017%.

TABLE 1

Class Distribution of Hydrocarbons in the 89.5-126° Fraction

Class of hydrocarbons	Number of hydro-carbons
Paraffins	19
Cyclopentanes	9
Cyclohexanes	8
Aromatic hydrocarbons	4

Engler Fractionation at 741.6 mm

Start of boiling 89.5°		90%	113.0°
10%	98.0°	95%	123.0°
50%	99.5°	End of boiling	126.0°

The fraction was accounted for to the extent of 91.4%. In all, 40 hydrocarbons were found in the fraction, and their contents were determined. Their distribution by classes is shown in Table 1.

The results of the analysis of the fractions are given in Table 2. The data in Table 2 make it possible to establish the group composition of the original fraction, which is given in Table 3.

A comparative analysis of the data presented in Tables 2 and 3 was made by us in the preceding communication [1].

The experiments on the reforming of the 89.5-126° fraction were carried out in a flow apparatus with recirculation of the gases [8] at a hydrogen pressure of 20 atm, $\underline{v}$ = 1.0 hour^{-1}, H_2 : HC = 12.6, 470-480°. The catalysis tube of the reactor was charged with 300 ml of catalyst. The required temperature of the catalyst was established gradually in a continuous stream of hydrogen in the course of four hours. The characterization of the catalyzate obtained in the reforming of the gasoline is given in Table 4 and in the figure. During the reforming of the fraction there was only a very small amount of gas formed, and the recirculating gas mixture contained up to 99% of hydrogen.

It follows from Table 4 and the figure that the content of aromatic hydrocarbons in the catalyzate is 26% after the first six hours of the work of the catalyst. In the catalyzate some broadening of the fractional composition was observed (boiling range 61-141°). At the same time the catalyst brought about almost complete desulfurization of the gasoline, for the sulfur content of the catalyzate was 0.001%, as compared with 0.017% in the original fraction.

The individual-hydrocarbon composition of the catalyzate obtained after the first five hours' work of the catalyst was determined by the combined method [7] •. The dearomatized part of the catalyzate was fractionated through a column of 75-plate efficiency. The results of the analysis of the catalyzate are presented in Table 5; it enabled us to establish the group composition of the catalyzate, as given in Table 6. It will be seen from a comparison of the group compositions of the original fraction and the catalyzate (Tables 3 and 6) that the catalyzate has a much-reduced content of cyclohexanes (18.5% in the original fraction and 1% in the

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• The Raman spectrum analysis of the catalyzate was carried out by Iu. P. Egorov, I. P. Iakovlev, and T. M. Ivanova, to whom the authors express their thanks.

catalyzate). The reduction in the content of cyclopentanes was also considerable: from 14.6% in the original fraction to 5.4% in the catalyzate. On the other hand, the relative amount of paraffins increased appreciably (61.8% in the catalyzate, as compared with 52.7% in the original fraction).

TABLE 2

Individual Hydrocarbons in the 89.5-126° Fraction

Hydrocarbon	Content	Hydrocarbon	Content
Paraffins			
Pentane	0.42	2-Methylhexane	4.62
Hexane	3.95	3-Methylhexane	5.23
2-Methylpentane	0.65	3-Ethylpentane	0.13
3-Methylpentane	1.01	Octane	4.33
2,2-Dimethylbutane	0.52	2,4-Dimethylhexane	0.75
2,3-Dimethylbutane	0.11	2-Methylheptane	3.68
Heptane	20.59	4-Methylheptane	3.03
2,2-Dimethylpentane	0.22	2,3,4-Trimethylpentane	0.75
2,3-Dimethylpentane	2.30	2,2,4-Trimethylhexane	0.14
2,4-Dimethylpentane	0.30		
		Total	52.7
Cyclopentanes			
Methylcyclopentane	1.18	cis-1,2-Dimethylcyclopentane	0.15
1,1-Dimethylcyclopentane	0.39	Ethylcyclopentane	1.19
trans-1,3-Dimethylcyclopentane	1.82	cis-trans-cis-1,2,3-Trimethyl-cyclopentane	1.01
cis-1,3-Dimethylcyclopentane	1.35		
trans-1,2-Dimethylcyclopentane	7.14	1,1,3-Trimethylcyclopentane	0.37
		Total	14.6
Cyclohexanes			
Cyclohexane	3.07	1.2-Dimethylcyclohexane	0.14
Methylcyclohexane	11.34	1.3-Dimethylcyclohexane	1.46
Ethylcyclohexane	0.68	1.4-Dimethylcyclohexane	0.64
1,1-Dimethylcyclohexane	0.07	1.13-Trimethylcyclohexane	1.08
		Total	18.5
Aromatic Hydrocarbons			
Benzene	0.47	Accounted for (% on original fraction)	91.4
Toluene	4.46		
m-Xylene	0.50	Residue in flask after fractionation	2.5
o-Xylene	0.21	Losses (%)	6.1
Total	5.6	Total	100.0

TABLE 3

Group Composition of the 89.5-126° Fraction

Class of hydrocarbons	Content (%)
Paraffins	52.7
Including	
normal	29.3
paraffins with a "3°" carbon atom	22.5
paraffins with a "4°" carbon atom	0.9
Cyclopentanes	14.6
Cyclohexanes	18.5
Aromatic hydrocarbons	5.6

It should be noted that the increase in the amount of paraffins is to be attributed mainly to increase in the amount of hydrocarbons having a tertiary carbon atom (29.3% in the catalyzate instead of 22.5% in the original fraction) and of those containing a quaternary carbon atom (5.6% instead of 0.9%). There was a considerable increase also in the amount of aromatic hydrocarbons (from 5.6% to 24.8%). Hence, comparison of the group compositions of the original fraction and the catalyzate indicates fairly profound reforming of the fraction over the sulfurized palladium catalyst, and in this process all classes of hydrocarbons undergo transformations.

It must be pointed out that the group composition of the catalyzate obtained in the reforming of the gasoline over a 0.5% $Pd-Al_2O_3$ catalyst treated with HF but not with H_2S (see [1]) differs from that of the present catalyzate. Thus, in the first catalyzate there was a somewhat higher content of aromatic hydrocarbons (26.4% instead of 24.8%) and a lower content of cyclopentanes (4.4% instead of 5.4%). The content of cyclohexanes was the same (about 1%) in both catalyzates. The increase in the amount of paraffins was about the same in two cases (62.3% instead of 61.8%). However, whereas in the first catalyzate there was a considerable increase in the amount of hydrocarbons having a tertiary carbon atom (by 12.1% instead of 6.8%), in the second the increase in the content of hydrocarbons having a quaternary carbon atom was more notable (by 4.7% instead of 1%).

TABLE 4

Characterization of the Catalyzate Obtained in the Reforming of the 89.5-126° Fraction

Time of run over catalyst (hours)	n_D^{20}	d^{20}	Content of aromatic hydrocarbons (%)	Time of run over catalyst (hours)	n_D^{20}	d^{20}	Content of aromatic hydrocarbons (%)
6,0	1.4145	0.729	26.0	44.0	1.4080	0.720	15.0
9,0	1.4140	0.728	25.0	54.0	1.4080	0.720	15.0
14,0	1.4110	0.725	19.0	59.5	1.4080	0.720	15.0
18,0	1.4100	0.725	18.5	64.0	1.4080	0.720	15.0
23,5	1.4090	0.723	17.0	73.0	1.4065	0.720	12.5
33,5	1.4085	0.723	15.5				

A comparison of Tables 2 and 5 shows that only C_5 and C_6 paraffins are present in the catalyzate in about the same amounts as in the original fraction. The same is observed also in the case of the first catalyzate, which was obtained over a nonsulfurized catalyst. Like the first catalyzate, this catalyzate contained seven isomeric C_7 hydrocarbons instead of six (in the original fraction). There were eight C_8 hydrocarbons instead of four (the first catalyzate contained eleven). Of the nine cyclopentane hydrocarbons in the original fraction seven still remained in this catalyzate (the first catalyzate contained only three). Of eight cyclohexanes, only three and two respectively remained in the catalyzates. In both catalyzates the number of aromatic hydrocarbons was increased from four to six.

Hence, although aromatization proceeded rather further on the nonsulfurized catalyst, possibly as a result of increased dehydroisomerization of cyclopentanes, the skeletal isomerization of paraffins proceeded to the same extent on both catalysts, the amount of hydrocarbons with a quaternary carbon atom being, however, somewhat greater over the sulfurized catalyst. It must be noted that the aromatizing power of the sulfurized palladium catalyst falls by only 20% in the course of 15 hours' work, whereas that of the nonsulfurized catalyst [1] falls by more than 40% in the same period. The content of aromatic hydrocarbons in the catalyzate falls to 12% after the reforming of the fraction has continued over the sulfurized catalyst for 73 hours, but over the nonsulfurized catalyst

TABLE 5

Individual Hydrocarbons in the Catalyzate from the 89.5 -126° Fraction of Volga-Urals Gasoline

Hydrocarbon	Content	Hydrocarbon	Content
Paraffins			
Pentane	0.43	Octane	4.34
Hexane	4.22	2,2-Dimethylhexane	1.33
2-Methylpentane	0.94	2,3-Dimethylhexane	1.33
3-Methylpentane	0.92	2,2,3-Trimethylpentane	1.43
2,2-Dimethylbutane	1.10	2,3,4-Trimethylpentane	0.16
Heptane	17.89	2-Methylheptane	1.54
2,2-Dimethylpentane	0.72	3-Methylheptane	1.40
2,3-Dimethylpentane	1.06	4-Methylheptane	2.94
2,4-Dimethylpentane	0.37	3-Ethylhexane	0.74
3,3-Dimethylpentane	0.65	2,2,5-Trimethylhexane	0.35
2-Methylhexane	10.56		
3-Methylhexane	7.19		
3-Ethylpentane	0.14	Total	61.8
Cyclopentanes			
Methylcyclopentane	1.74	trans-1,2-Dimethylcyclopentane	1.2
trans-1,3-Dimethylcyclopentane	0.46	cis-1,2-Dimethylcyclopentane	0.59
2,4-Dimethylcyclopentane	0.15	1,1,3-Trimethylcyclopentane	0.37
1,3-Dimethylcyclopentane	0.90		
		Total	5.4
Cyclopentanes			
Methylcyclohexane	0.78		
1,1-Dimethylcyclohexane	0.17		
1,4-Dimethylcyclohexane	0.05		
Total	1.00		
Aromatic Hydrocarbons			
Benzene	2.81	Accounted for (%)	93.0
Toluene	15.11	Residue in flask after fractionation (%)	2.3
m-Xylene	3.36		
o-Xylene	1.35	Losses (%)	4.7
p-Xylene	1.19		
Ethylbenzene	0.99	Total	100.0
Total	24.8		

that was treated with HF this fall requires only 45 hours. Moreover, when the fraction is re-formed over palladium catalyst that has been treated neither with HF nor with H_2S, the fall in the content of aromatic hydrocarbons to 12% requires only 27 hours' work by the catalyst [1].
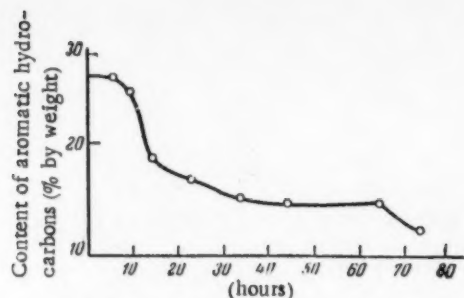
Change in the content of aromatic hydrocarbons in the catalyzate from the 89.5-126° fraction of Volga-Urals gasoline

TABLE 6

Group Composition of the Catalyzate from the 89.5-126° Fraction of Volga-Urals Gasoline

Class of hydrocarbons	Content (%)
Paraffins	61.8
Including	
normal	26.9
paraffins with a "3°" carbon atom	29.3
paraffins with a "4°" carbon atom	5.6
Cyclopentanes	5.4
Cyclohexanes	1.0
Aromatic hydrocarbons	24.8

SUMMARY

1. An investigation was made of the conditions of the reforming of the 89.5-126° fraction of gasoline from Volga-Urals petroleums at 470-480°, at 20 atm, at $\underline{v}$ = 1 hour^{-1}, and at H_2 : HC = 12.6 over palladized alumina (0.5% $Pd-Al_2O_3$) treated with HF and H_2S.

2. Under these conditions the catalyst brings about dehydrogenation of cyclohexanes, dehydroisomerization of cyclopentanes, skeletal isomerization of paraffins, and desulfurization of the gasoline.

3. A catalyst consisting of 0.5% of Pd on Al_2O_3 and given a preliminary treatment with hydrogen sulfide was found to be more stable toward organic sulfur compounds than palladium catalysts that had not been treated with hydrogen sulfide.

4. The individual-hydrocarbon compositions of the original fraction and the catalyzate were investigated by the combined method.

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* Original Russian pagination. See C. B. Translation.

** Russian translation.

HETEROGENEOUS CATALYTIC DEHYDROGENATION OF ISOPENTANE
AS A FUNCTION OF TEMPERATURE

N. I. Shuikin, E. A. Timofeeva, and T. P. Dobrynina

We have previous investigated [1] the effect of temperature on the dehydrogenation of n-pentane in presence of an alumina-chromia-potassia catalyst. It was shown that the dehydrogenation of n-pentane attains an equilibrium state at 500-550°. We therefore decided to carry out an analogous investigation with isopentane.

EXPERIMENTAL

The experiments were carried out with the same portion of catalyst (30 ml) and under the same conditions as the experiments on n-pentane. The catalyst had the same activity as in the work on n-pentane. The temperature range selected was 500-575°, because at lower temperatures the alimina-chromia-potassia catalyst was found to have low activity in the dehydrogenation of n-pentane; a space velocity of 0.5 hour^{-1} was used. Before the experiments the catalyst was heated to the required temperature in a stream of air, air was displaced by nitrogen, and the catalyst was then treated with hydrogen for 90 minutes. In each experiment, reaction was allowed to occur over the catalyst for one hour, and the catalyzate and gas were collected during the last 43-44 minutes.
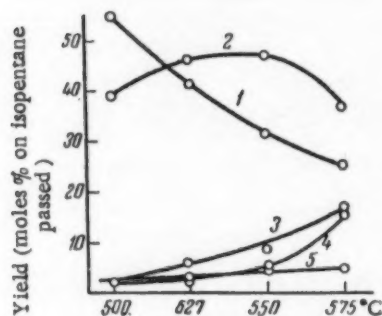
Fig. 1. Yields of reaction products as functions of temperature: 1) isopentane; 2) isopentenes; 3) coke; 4) gas; 5) isoprene
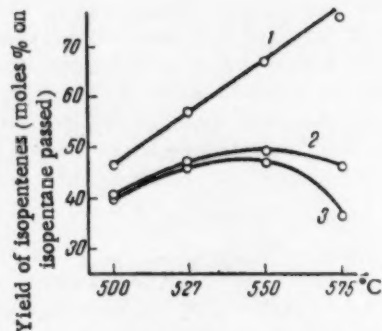
Fig. 2. Equilibrium and experimental yields of isopentanes as functions of temperature: 1) equilibrium concentrations (according to Equation 1); 2) equilibrium concentrations (according to Equation 2); 3) experimental yields

Before the experiment about 2.3 g of isopentane was passed over the catalyst, and during the experiment 6.23 g was passed. The procedure is described in greater detail in our previous paper [1]. In the experiments with isopentane, as in those with n-pentane, the gross total in the gravimetric balance varied in the range 98-102%. On the basis of these results, the molar balance was calculated by the formulas given previously [1].

TABLE 1

Thermodynamic Calculation of the Dehydrogenation Reaction Isopentane ⇌ Isopentenes

Hydrocarbon	600° K — 327° C		700° K — 427° C		800° K — 527° C		900° K — 627°	
	K_p	x	K_p	x	K_p	x	K_p	x
2-Methyl-1-butene	0.00044	2.1	0.01462	12.0	0.20880	41.6	1.67260	79.1
3-Methyl-1-butene	0.00004	0.7	0.00184	4.3	0.03225	17.7	0.30230	48.2
2-Methyl-2-butene	0.00084	2.9	0.02215	14.7	0.25540	45.1	1.73940	79.7
All isopentenes	0.00132	3.6	0.03861	19.3	0.49645	57.6	3.71430	88.8

TABLE 2

Effect of Temperature on the Properties of the Liquid Catalyzate and on the Composition of the Gas

Experiment	Temperature of exp.	Yield of liquid catalyzate (%)	Amount of gas (liters at STP)	Properties of catalyzate			Isoprene content	Composition of gas (% by volume)				Composition of "coke"
				n_D^{20}	Iodine value	Content of isopentenes (%)		H_2	C_nH_{2n}	C_nH_{2n+2}	Carbon number	
1	500	93.8	1.010	1.3654	153.2	40.4	1.5	91.6	0.4	8.0	1.6	$C_{1.0}H_1$
2		94.9	1.010	1.3660	154.8	40.9		90.0	0.4	9.6	—	$C_{1.1}H_1$
3	527	87.8	1.663	1.3700	193.0	50.2	2.5	87.5	1.0	11.5	1.5	$C_{2.4}H_1$
4		90.0	1.606	1.3708	193.3	50.3		87.7	1.2	11.1	—	$C_{2.3}H_1$
5	550	83.8	2.173	1.3745	226.3	55.8	5.5	79.6	3.0	17.4	1.6	$C_{2.5}H_1$
6		80.9	2.123	1.3750	222.9	54.9		81.3	2.2	16.5	—	$C_{3.6}H_1$
7	575	67.1	3.142	1.3800	227.7	54.2	7.1	68.7	5.4	25.9	1.6	$C_{3.7}H_1$
8		67.2	2.895	1.3805	223.6	53.1		68.5	4.7	26.8	—	$C_{3.0}H_1$

TABLE 3

Effect of Temperature on the Yields of Reaction Products and the Selectivity of the Catalyst

(moles % on isopentane passed)

Temperature (°C)	Unchanged iso-pentane	Iso-pentenes	Iso-prene	Amount of isopentane converted into		Total	Selectivity
				"coke"	gas		
500	55	39	2	2	2	100	90
527	42	46	2	6	3	99	83
550	32	47	5	9	6	99	80
575	26	37	5	17	16	101	57

TABLE 4

Experimental and Equilibrium Yields at Various Temperatures

Experiment	Temperature	Reaction products (mole fractions)					K_p	Equilibrium concentrations of C_5H_{10} ($\underline{x}$)	
		C_5H_{12} n_1	C_5H_{10} n_2	H_2 n_3	gas + iso-prene n_4	Σn_i		according to Equation (1)	according to Equation (2)
1	500	0.545	0.390	0.477	0.063	1.475	0.27230	0.463	0.418
2		0.546	0.400	0.465	0.068	1.479			0.410
3	527	0.416	0.453	0.751	0.132	1.752	0.49645	0.576	0.464
4		0.425	0.466	0.727	0.123	1.741			0.481
5	550	0.325	0.481	0.792	0.263	1.861	0.80350	0.672	0.523
6		0.320	0.461	0.908	0.236	1.925			0.491
7	575	0.260	0.373	1.113	0.558	2.304	1.39600	0.763	0.463
8		0.267	0.368	1.023	0.522	2.180			0.469

The iodine values of the catalyzates were determined by the bromometric method described by Gal'pern [2], and the isoprene contents were determined gravimetrically with the aid of maleic anhydride; in this procedure, which was described by Guliaeva, Polikarpova, and Remiz [3], we made some modifications and improvements: the catalyzate was distilled from the heavy residue (from the start of boiling to 40°), and the distillate was heated with maleic anhydride in a sealed tube in a thermostat at 70° for three hours. When cool, the tube was opened without loss of glass, and substance that had not reacted with maleic anhydride was drawn off at the pump. As a rule pumping for six hours was necessary for the attainment of constant weight.

The content of isopentenes was calculated from the formula [4]:

$$H = \frac{N \cdot 70}{254} - 1,2 D;$$

in which H is the isopentene content (%), N is the iodine value, 70 is the molecular weight of isopentene, 254 is the molecular weight of iodine, D is the isoprene content (%), and 1.2 is an experimental coefficient. Equilibrium concentrations were determined from the equation:

$$K_p = \frac{x^2}{1 - x^2}, \tag{1}$$

and, taking account of side reactions, from the equation:

$$K_p = \frac{x(n_3 - n_2 + x)}{(n_1 + n_2 - x)(\Sigma n_i - n_2 + x)}, \tag{2}$$

in which K_p is the equilibrium constant, $\underline{x}$ is the yield of isopentenes, $\underline{n}$ is mole fraction of reaction product (n_1 for unchanged isopentane, n_2 for isopentenes, n_3 for hydrogen, and n_4 for gaseous hydrocarbons and isoprene; $\Sigma n_i = n_1 + n_2 + n_3 + n_4$). The values of K_p in Table 4 were found graphically by extrapolation from data in Table 1, which were calculated from values of the free energies of formation of isopentenes [5]. The yields of isopentenes ($\underline{x}$) in Table 1 were calculated from Equation (1).

The results are presented in Tables 2-4 and Figures 1 and 2.

From the experimental results it follows that the experimental yields of isopentenes in the temperature range 500-550° almost attain equilibrium value with a catalyst selectivity of 57 moles %.

The dehydrogenation of n-pentane under the same conditions and in the same temperature range also attained equilibrium [1]. However, the absolute yields of isopentenes were 7-8% higher than those of n-pentenes. The selectivity of the catalyst for the dehydrogenation of isopentane was also considerably higher than for the dehydrogenation of n-pentane. Under the given conditions, coke and gas formation occurred to a lesser extent in the dehydrogenation of isopentane than in the dehydrogenation of n-pentane, but in both cases more hydrocarbon was converted into coke than into gas.

Hence, the extent of the dehydrogenation of isopentane is greater than that of n-pentane under identical conditions. This conclusion is in complete accord with thermodynamic calculations given in the previous communication [1] and in the present paper (Table 1).

SUMMARY

1. An investigation was made of the effect of temperature on the dehydrogenation of isopentane in presence of an alumina-chromia-potassia catalyst at a space velocity of 0.5 hour^{-1}.

2. In the range 500-550°, with the given extent of side reactions, the dehydrogenation of isopentane attains an equilibrium state.

3. At 500-550° the yield of isopentenes from isopentane is 7-8 moles per cent greater than that of pentenes from n-pentane.

4. Under the given conditions, less "coke" and gas is formed in the dehydrogenation of isopentane than in the dehydrogenation of n-pentane.

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* Original Russian pagination. See C. B. Translation.

** In Russian.

ISOMERIZATION OF SATURATED HYDROCARBONS
COMMUNICATION 3. ISOMERIZATIONS OF CYCLOALKANES

Al. A. Petrov, S. R. Sergienko, A. L. Tsedilina, A. N. Kislinskii, and G. D. Gal'pern

In previous communications [1,2] we examined the isomerization of paraffins in presence of multifunctional catalysts and of hydrogen under pressure. The present paper is devoted to a study of the reactions of cycloalkanes under the same conditions. There are several published papers on the transformations of cycloalkanes in presence of bifunctional catalysts [3-6]. However, in most investigations, apart from the work of Ciapetta [3] which was carried out on comparatively few individual hydrocarbons, attention has been focused mainly on aromatization. In any case, these investigations were carried out under conditions that favored the formation of aromatic hydrocarbons in substantial amount.

As in the case of paraffins, the main object of the present work was the study of the regularities observed in the isomerization of hydrocarbons and of the relationship between their structures and the kinetic and thermodynamic parameters of their reactivities.

EXPERIMENTAL

The isomerization of the cycloalkanes was carried out in a flow system under pressure, in the apparatus described in the previous papers [1,2]. The experimental conditions were: pressure 25 atm; space velocity 1.0 hour $^{-1}$; molar ratio of hydrogen to cycloalkane 4; temperature 370° in the case of C_6H_{12} and C_7H_{14} and 360° in the case of C_8H_{16} and C_9H_{18}. Practically no hydrocracking was observed in the experiments with C_6-C_8 cycloalkanes, but in the case of C_9H_{18} cycloalkanes the catalyzate contained about 10% of liquid products that boiled below the start of boiling of the C_9 fraction. The amounts of paraffins formed by the hydrogenolysis of cyclopentanes were 2-3% in the catalyzate from C_6H_{12} cycloalkanes and 7-8% for C_7H_{14} cycloalkanes (according to the aniline points). Under these conditions the extent of hydrogenolysis appears to be independent of the structure of the original hydrocarbon, but it tends to increase with increase in the molecular weight of the hydrocarbon. The contents of aromatic hydrocarbons in the catalyzates did not exceed 1-3% and, under given conditions, they also increased with increase in the molecular weight of the original hydrocarbon.

As in the preceding investigation [1], the catalyst used was a platinized aluminum silicate (0.5% Pt) of the Houdry type. In presence of this catalyst at 370°, 25 atm, and a space velocity of 1.0 hour $^{-1}$, cyclohexane was isomerized into methylcyclopentane to the extent of 90-92%, an equilibrium mixture being formed. The compositions of the transformation products from cycloalkanes were investigated mainly with the aid of Raman spectra. The details of the spectrum analysis were described previously [1]. In order to improve the accuracy of the determination of the concentrations of individual C_7H_{14} hydrocarbons in the isomerizates, the spectra of 1,2- and 1,3-dimethylcyclopentanes were determined under the same conditions. As the C_8H_{16} and C_9H_{18} isomerizates were fairly complex mixtures, they were first dehydrogenated over platinized charcoal at 305°, and the lower-boiling cyclopentane hydrocarbons were then separated by fractionation through a column of 15-plate efficiency. The aromatized residues and the cyclopentanes that had been distilled off were also investigated with the aid of Raman spectra. It will be clear that data obtained in this way refer only to the structural forms of the cyclohexanes in the catalyzates without any distinction between geometric isomers; at the same time the accuracy of the analysis was considerably increased because of the brightness of the lines due to the aromatic hydrocarbons. Also, the total content of cyclohexanes, apart from gem-substituted cyclohexanes, was determined in all isomerizates by dehydrogenation over platinized charcoal at 305° with subsequent absorption of the aromatic hydrocarbons in 98% sulfuric acid.

Properties of Hydrocarbons used in Work

Hydrocarbon	B.p. (°C)	n_D^{20}	d_4^{20}	Method of preparation
Methylcyclohexane	101—101.5	1.4227	0.7687	Hydrogenation of toluene
1,1-Dimethylcyclopentane	87.5—88	1.4136	0.7551	See text
1,2-Dimethylcyclopentane	96—98	1.4177	0.7637	From methylmagnesium iodide and 2-methylcyclopentanone
1,3-Dimethylcyclopentane	90.7—91.2	1.4094	0.7449	From methylmagnesium iodide and 3-methylcyclopentanone
Ethylcyclopentane	102.5—103	1.4199	0.7655	From ethylmagnesium bromide and cyclopentanone
1,2-Dimethylcyclohexane	126—127	1.4327	0.7890	From methylmagnesium iodide and 2-methylcyclohexanone
1,3-Dimethylcyclohexane	120—121	1.4261	0.7762	From methylmagnesium iodide and 3-methylcyclohexanone
1,4-Dimethylcyclohexane	121—121.5	1.4260	0.7760	From methylmagnesium iodide and 4-methylcyclohexanone
Ethylcyclohexane	131—131.5	1.4333	0.7878	From ethylmagnesium bromide and cyclohexanone
Propylcyclopentane	129—130	1.4258	0.7746	From propylmagnesium bromide and cyclopentanone
Propylcyclohexane	154—156	1.4372	0.7983	From butylmagnesium bromide and cyclohexanone
Butylcyclopentane	152—153	1.4305	0.7830	From butylmagnesium bromide and cyclopentanone

TABLE 2

Isomeric Transformations of C_7H_{14} Cycloalkanes

Original Hydrocarbon	Composition of isomerization products (%)[*]								
	Methylcyclohexane	1,2-Dimethylcyclopentane (cis)	1,2-Dimethylcyclopentane (trans)	Σ1,2-Dimethylcyclopentanes	1,3-Dimethylcyclopentane (cis)	1,3-Dimethylcyclopentane (trans)	Σ1,3-Dimethylcyclopentanes	1,1-Dimethylcyclopentane	Ethylcyclopentane
Methylcyclohexane[**]	31 (28)	—	—	24	—	—	26	9	10
1,2-Dimethylcyclopentane	25	7	20	27	8	15	23	10	15
1,3-Dimethylcyclopentane	23	5	23	28	7	18	25	10	15
1,1-Dimethylcyclopentane	26	5	20	25	5	19	24	10	15
Ethylcyclopentane	24	7	21	28	8	15	23	10	15
Equilibrium state at 377° (according to Rossini)	35	2	18	20	8	16	24	8	13

[*] The Raman spectrum results were accurate within about 10%.

[**] According to Ciapetta's results [3]. The result in parentheses was obtained by us.

The hydrocarbons used were mainly obtained synthetically by the Grignard reaction. The tertiary alcohols obtained were dehydrated over pure alumina at 280°. The cycloalkanes were then hydrogenated in an autoclave over Raney nickel at 170-180° and 100-120 atm. The properties of the hydrocarbons and the methods by which they were prepared are given in Table 1. We shall discuss here only the rather complicated way in which 1,1-dimethylcyclopentane was prepared. The starting material was commercial dimedone, 5,5-dimethyl-1,3-cyclohexanedione. The diketone was hydrogenated in alcoholic solution in an autoclave over Raney nickel at 200-210° and 180-200 atm. Under these conditions 3,3-dimethylcyclohexanol was obtained in 70% yield. This alcohol was oxidized with alkaline permanganate at 30-40°. The resulting mixture of 2,2- and 3,3-dimethyladipic acids (with predominance of the latter) was cyclized by heating it with barium carbonate and gave a mixture of dimethylcyclopentanones. These ketones were converted into their hydrazones, which were heated with potas-

TABLE 3

Isomeric Transformations of C_8H_{16} and C_9H_{18} Cycloalkanes

Original Hydrocarbons	Composition of isomerization products (%)						Data on the composition of cyclopentanes
	Σ Cyclohexanes (without gem substituted)	Relative concentrations of cyclohexane					
		Dimethylcyclohexanes				Ethylcyclohexanes	
		1.1-	1.2-	1.3-	1.4-		
1,2-Dimethylcyclohexane	28	10	20	35	25	10	Mainly various geometric isomers of 1,2,4-trimethylcyclopentane*
1,3-Dimethylcyclohexane	33	10	20	35	25	10	
1,4-Dimethylcyclohexane	30	10	20	35	25	10	
Ethylcyclohexane	36	10	10	20	10	50	
Propylcyclopentane	33	10	10	20	10	50	
Equilibrium composition of C_8H_{16} cyclohexanes at 327° (according to Rossini)	—	7	18	43	22	10	
Propylcyclohexane	33	1,2,4-Trimethylcyclohexane				60 }	—
		1,3,5-Trimethylcyclohexane				20 } *	
		Σ Ethylmethylcyclohexanes				20 }	
Butylcyclopentane	30	—				—	—
Equilibrium composition of C_9H_{12} aromatic hydrocarbons at 327° (according to Rossini)		1,2,4-Trimethylbenzene				45	—
		1,3,5-trimethylbenzene				17	
		Σ Ethylmethylbenzenes				16	

* Analyses on these products were carried out by Iu. P. Egorov in the Institute of Organic Chemistry of the Academy of Sciences of the USSR.

sium hydroxide and pieces of platinized clay (Kizhner's method) with formation of the required 1,1-dimethylcyclopentane.

The results of experiments on the isomerization of 12 individual cycloalkanes of composition C_7-C_9 are given in Tables 2 and 3. From these tables it will be seen that the isomeric transformations of cycloalkanes of various structures are in general fairly rapid and the compositions of the final reaction products are in good agreement with the calculated thermodynamic values [7, 8] (detailed data of the spectrum analyses of various isomerizates are given in Tables 4 and 5). In view of the absence of data on the equilibrium composition for C_9H_{18} cyclohexanes, we have cited values for the equilibrium concentrations of the corresponding benzene homologs [9].

As a general rule, in the isomeric transformations of cycloalkanes a predominance of cyclopentanes in the catalyzates is to be noted, and for C_7 and higher cycloalkanes the content of cyclopentanes is fairly constant, the limits of variation being 23-33%. Approximately the same proportions were found by us previously in the study of the isomerization of cycloalkenes [10]. With respect to the character of the change in the structure of the hydrocarbon skeleton, the isomeric transformations of cycloalkanes can be divided into three groups:
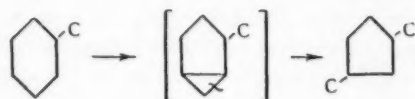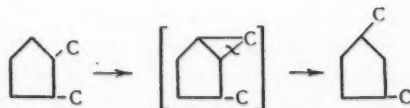
TABLE 4

Raman Spectra[*] of C_7H_{14} Catalyzates

Original C_7H_{14} hydrocarbon							
1,2-Di-methyl-cyclopen-tane	1,3-Di-methyl-cyclopen-tane	1,1-Di-methyl-cyclopen-tane	Ethyl-cyclo-pentane	1,2-Di-methyl-cyclopen-tane	1,3-Di-methyl-cyclopen-tane	1,1-Di-methyl-cyclopen-tane	Ethyl-cyclo-pentane
Spectra of catalyzates							
218 (0)	212 (0)	210 (0)	219 (0)	956 (0)	953 (0,5)	949 (0)	954 (0,5)
264 (0)	264 (0)?	260 (0)	260 (0)	976 (2 b)	975 (1 b)	974 (1,5 b)	974 (2,5 b)
317 (0)	—	309 (0)	310 (0)	—	—	990 (0)	987 (0)
338 (0)?	—	344 (0)?	340 (0)	1002 (2,5)	1003 (3)	1003 (3)	1003 (2,5)
—	—	—	385 (0)	—	1014 (0)	—	1017 (0)
407 (1)	407 (0,5)	406 (1)	408 (1)	1030 (6)	1031 (5)	1030 (5,5)	1032 (6,5)
—	421 (0)?	424 (0)	421 (0)	1058 (1)	1062 (0)	1059 (0)	1057 (0,5)
446 (2)	446 (1)	445 (2)	447 (2)	1085 (2,5 b)	1084 (2 b)	1084 (2,5 b)	1088 (2,5 b)
472 (0)	469 (0)	466 (0)	—	—	1123 (0)	1127 (0)	1128 (0)
494 (1,5)	497 (1,5)	495 (1,5)	499 (1)	1145 (2,5)	1144 (2)	1144 (2)	1145 (1)
520 (1)	519 (1)	520 (1)	520 (1)	1162 (2,5)	1162 (2)	1159 (2)	1163 (2)
531 (0)	—	532 (0)	—	1187 (0)	1193 (0)	1196 (0)	1193 (0,5)
544 (2)	546 (1,5)	545 (2)	545 (2)	1207 (2)	1208 (2)	1208 (1)	1209 (2)
560 (0)	561 (0)?	559 (0,5)	561 (0,5)	1227 (0)	1221 (0)	1225 (0)	1232 (0)
610 (0)	—	609 (0)	—	1249 (3)	1250 (2)	1249 (2)	1249 (1,5)
—	625 (0)	620 (0)	625 (0)	1264 (3)	1264 (3)	1264 (3)	1264 (3,5)
—	684 (0)	683 (0)	686 (0)	1285 (0)	—	—	1287 (0)
751 (0)	756 (0,5)	755 (0)	751 (0)	1305 (1,5)	1305 (2)	1304 (1,5)	1305 (1,5)
770 (8)	770 (7)	769 (6)	770 (8)	1345 (3 b)	1344 (3 b)	1344 (2,5 b)	1344 (4)
786 (1)	787 (1)	786 (1)	787 (1)	—	1364 (0)	—	1362 (0,5)
803 (1,5)	803 (1)	802 (2)	803 (1)	1382 (0)	1386 (0)	1382 (0)	1384 (0)
827 (0,5)	827 (0,5)	825 (0,5)	825 (0,5)	1403 (0)	1402 (0)?	1403 (0)	1397 (0)
844 (2)	843 (1,5)	843 (1,5)	844 (2,5)	1454 (10 b)	1454 (10b)	1453 (10 b)	1455 (10 b)
866 (0)	870 (0)	864 (0)	863 (0)	1593 (0)	1580 (0)?	1585 (0)	1582 (0)
890 (3,6b)	895 (3,5 b)	892 (3,5 b)	894 (3,5 b)	1606 (0)	1612 (0)	1600 (0,5)	1610 (0,5)
938 (0)	936 (0)	—	930 (0)	1680 (0)	—	—	1686 (0)?

[*] The frequencies of the spectrum lines are given in cm^{-1}; the figures in parentheses are intensities on a ten-degree scale; b indicates broad line.

1) change in the number of carbon atoms in the ring:

2) displacement of methyl radicals in the ring:

3) isomerization of alkyl groups, as a result of which polysubstituted cycloalkanes are formed:
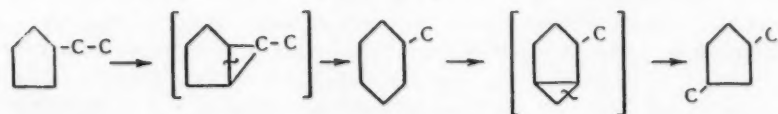
TABLE 5

Raman Spectra*of C_8H_{16} Catalyzates (after dehydrogenation)

Original C_8H_{16} Catalyzates									
1,2-Di-methyl-cyclo-hexane	1,3-Di-methyl-cyclo-hexane	1,4-Di-methyl-cyclo-hexane	Ethyl-cyclo-hexane	Propyl-cyclo-pentane	1,2-Di-methyl-cyclo-hexane	1,3-Di-methyl-cyclo-hexane	1,4-Di-methyl-cyclo-hexane	Ethyl-cyclo-hexane	Propyl-cyclo-pentane
Spectra of catalyzates									
201 (0)	210 (0,5)	204 (1)	204 (0)	—		—	—	761 (0)	760 (1)
224 (2)	227 (4)	227 (3)	227 (2)	224 (0,5)	770 (1)	770 (1)	770 (1)	770 (3.5)	770 (3.5)
252 (0,5)	255 (0.5)	252 (0)	252 (0)	253 (0)	789 (0)	794 (0)	794 (0)	—	791 (0)
276 (1)	276 (1)	278 (1)	279 (1)	281 (0)	811 (1.5)	811 (1.5)	811 (2)	810 (1)	812 (0.5)
310 (1)	312 (1.5)	314 (2)	314 (2)	315 (0)	830 (5)	829 (5.5)	830 (7.5)	830 (3.5)	830 (1)
—	345 (0)	339 (0)	335 (0)	335 (0)	856 (0)	—	858 (0)	—	855 (0)
—	383 (0)	383 (0)	387 (0)	390 (0)	898 (0)	900 (0)	896 (0)	900 (0)	898 (0)
406 (0)	402 (0)	408 (0)	408 (0)	410 (0 5)	967 (0)	971 (0)	966 (0.5)	971 (1)	965 (0)
417 (0)	420 (0)	424 (0)	—	422 (0,5)	—	—	982 (0)	—	981 (0)
436 (0)	440 (0)	436 (0)	433 (0)	445 (0)	999 (10)	1000 (10)	1000 (10)	1001 (10)	1002 (8.5)
450 (2,5)	459 (2.5)	460 (3.5)	458 (2.5)	460 (1 b)	1031 (2)	1033 (2)	1033 (1.5)	1030 (4)	1030 (3)
480 (0)	485 (0)	480 (0)	483 (0)	485 (0.5)	1053 (3.5)	1054 (1)	1054 (3)	1053 (2.5)	1060 (2,5)
500 (0)	—	—	498 (0)	497 (1)	1075 (0)	1078 (0)	1072 (0)	1070 (0)	1093 (0)
513 (2,5)	516 (3)	517 (3.5)	516 (2.5)	519 (1)	1095 (0.5)	1097 (1)	1098 (1)	1097 (0.5)	—
536 (5,5)	537 (5.5)	537 (6)	536 (5)	539 (2)	1157 (0.5)	1161 (0.5)	1161 (1)	1158 (1)	1160 (1)
557 (0)	549 (0)	548 (0)	—	545 (1.5)	1171 (0)	1172 (0)	1174 (0)	1175 (0)	1167 (1)
581 (3)	566 (0)	—	560 (0)	560 (0.5)	1187 (0.5)	1186 (0.5)	1187 (0.5)	1187 (0,5)	1188 (0)
604 (0)	583 (3)	583 (3)	582 (2.5)	583 (1)	1205 (5)	1205 (4.5)	1206 (5)	1205 (5,5)	1207 (1.5)
624 (0,5)	606 (0)	610 (0)	—	606 (0)	1223 (3.5)	1225 (3)	1224 (2.5)	1225 (1)	1225 (1)
645 (2)	623 (0.5)	626 (0.5)	623 (2.5)	623 (1)	1251 (4.5)	1251 (4.5)	1251 (4)	1251 (3)	1250 (1.5)
669 (0)	645 (2)	646 (2)	645 (1.5)	648 (0.5)	1265 (1)	1266 (0.5)	1266 (1)	1266 (0,5)	1266 (0,5)
703 (0,5)	667 (0)	668 (0)	669 (0)	668 (0)	1312 (0)	1311 (0)	1311 (1)	1314 (0)	1307 (1)
726 (9)	683 (0)	682 (0)?	683 (0)	689 (0)	1351 (0)	1347 (0)	1350 (0)	1350 (0)	1347 (2 b)
733 (8)	704 (1)	702 (0.5)	705 (0.5)	706 (1)	1380 (7,5)	1381 (7,5)	1381 (8)	1382 (7.5)	1381 (2) b)
749 (0,5)	726 (8.5)	727 (9)	726 (8)	727 (3)	1452 (6 b)	1452 (7 b)	1455 (6 b)	1453 (5.5 b)	1456 (10 b)
	734 (5)	735 (5)	734 (4.5)	735 (1)	1588 (1)	1590 (1)	1590 (1)	1584 (1)	1590 (0)
	751 (0)	750 (0)	750 (0.5)	751 (1.5)	1615 (6.5)	1619 (5.5)	1619 (5.5)	1616 (6.5)	1616 (2)

* The footnote to Table 4 also applies here.

We shall not give a detailed discussion of the mechanism of these transformations because this has already been discussed by us in some detail in previous papers on the isomerization of cycloalkenes [10,11]. We will state only that here, as in the case of paraffins [1], we consider the primary act in the isomerization is the formation (by dehydrogenation) of a cycloalkene, which is the species that undergoes direct isomerization.

We considered it to be of greater interest to discuss some matters associated with the part played by hydrogen and by pressure in the reactions of cycloalkanes on a multifunctional catalyst. In our previous paper on the isomerization of paraffins we have already pointed out two main functions of pressure (and hydrogen): reduction in the equilibrium concentration of unsaturated hydrocarbons and increase in the rate of their hydrogenation. In the case of the isomerization of cycloalkanes these two functions must be supplemented by a third: reduction in the equilibrium concentration of aromatic hydrocarbons.

As is well know, equilibrium in the reaction cyclohexanes ⇌ aromatic hydrocarbons at atmospheric pressure is almost completely on the side of the aromatic hydrocarbons at 300°. On the other hand, at a comparatively low pressure (25 atm) equilibrium moves toward the cycloalkanes even at higher temperatures (370°). Various papers have appeared in which equilibrium constants have been calculated for the hydrogenation of benzene and dehydrogenation of cyclohexane experimentally under the conditions of our experiments. In both cases at 370° and 10 atm we obtained a catalyzate containing 25-27% of benzene, which is in general agreement with the calculated values of Frost [12]. Detailed calculations of equilibrium concentrations for the hydrogenation of benzene and its homologs and also data on the effect of an excess of hydrogen on the degree of hydrogenation can be found in [13]. From this it will be seen that the catalytic transformations of cycloalkanes into aromatic hydrocarbons in presence of a bifunctional catalyst constitute a fairly flexible process, capable of being directed, according to the temperature and pressure, either toward the formation of cycloalkanes or toward the formation of aromatic hydrocarbons. This fact is of great practical importance and is at present utilized in works practice. Moreover, it is only by a combination of isomerization and dehydrogenation that it is possible to convert not only cyclohexanes, but also most cyclopentanes, into aromatic hydrocarbons.

A characteristic example of simultaneous isomerization and dehydrogenation is the process of dehydroisomerization of methylcyclopentane into benzene, which probably proceeds as follows:


The view that methylcyclopentene and cyclohexene are formed as intermediate products was advanced by Mills and Heineman [14]. Under these conditions the yield of benzene in one passage attains 50% in spite of the fact that the first two stages are energetically very disadvantageous, with equilibrium concentrations of products of not more than a few per cent. We have intentionally discussed this example in detail as being characteristic of the reactions of hydrocarbons over multifunctional catalysts because it is of great importance to realize that reaction proceeds through a series of intermediaries whose formation is sometimes thermodynamically very disadvantageous, though this effect is made up for in the general energy gain in the conversion of the original hydrocarbon into the final product. It will be understood that, in view of their low concentrations, the formation of such intermediaries is not contrary to thermodynamic principles.

We studied also the dehydroisomerization of cyclopentanes for the transformations of various geometric isomers of 1,2,4-trimethylcyclopentane isolated from dehydrogenated catalyzates of trimethylcyclohexanes (Table 3). It was found that in presence of platinized aluminum silicate at 470° and 15 atm these cycloalkanes gave 70% of aromatic hydrocarbons. On the other hand, at 370° and 25 atm the amount of aromatic hydrocarbons formed did not exceed a few per cent and the catalyzate contained 23% of cyclohexanes.

We must consider the dehydrogenation of cyclohexanes under the conditions of the present work in somewhat greater detail. According to Balandin's multiplet theory [15], the dehydrogenation of cyclohexanes and the hydrogenation of aromatic hydrocarbons in presence of platinum catalysts proceed in one stage without the intermediate formation of cycloalkenes and cycloalkadienes. On the other hand, over oxide catalysts (e.g. chromium oxide) dehydrogenation proceeds with an edgewise orientation of the molecule and the formation of unsaturated hydrocarbons as intermediate products.

We consider that on platinized multifunctional catalysts, including the platinized aluminum silicate used in the present work, the dehydrogenation of cyclohexanes and the hydrogenation of aromatic hydrocarbons again proceed in stages, i.e., with intermediate formation of cycloalkenes and cycloalkadienes. The concentrations and lives of these intermediaries are insignificant and by the use of only a hydrogenating-dehydrogenating cata-lyst it is impossible to detect their formation because the rates of dehydrogenation and hydrogenation of cycloalkenes and cycloalkadienes are apparently considerably greater than those of the dehydrogenation of cycloalkanes and the hydrogenation of aromatic hydrocarbons. When use is made of a multifunctional catalyst which has an acidic component capable of acting in other directions on unsaturated hydrocarbons (the rates of these reactions are very high because of their ionic character), it is sometimes possible to detect the formation of such compounds. Apart from the above example of the isomerization of cycloalkanes, which requires the formation of unsaturated hydrocarbons as intermediate products, we observed also that the hydrogenation of benzene over platinized aluminum silicate at 370° and 10 atm in presence of a deficiency of hydrogen (molar ratio hydrogen : benzene = 0.1-0.2) is accompanied by coke formation on the catalyst and the appearance in the catalyzate of high-boiling fluorescent compounds, i.e., products such as are generally formed in the catalytic treatment of cyclohexene with pure aluminum silicate. It is clear that the difficulties artificially created in the hydrogenation of benzene (and also of cyclohexene and cyclohexadiene) have here favored a longer period of existence for the intermediate unsaturated hydrocarbons. It should be noted that the view that the dehydrogenation of cyclohexane in presence of nickel supported on aluminum silicate proceeds in stages was advanced also in the above-cited paper by Mills and co-workers on the mechanism of the isomerization of saturated hydrocarbons [4]; it was suggested also in an earlier paper by Kagan [16].

In conclusion we shall discuss the relative rates of isomerization of some cycloalkanes. It will be seen from the data in Table 3 that catalyzates obtained in experiments on the isomerization of ethylcyclohexane and propylcyclopentane contain a relatively large amount of the first of these hydrocarbons. An explanation of this should probably be sought in the slow isomerization of ethylcyclohexane, as compared with that of dimethylcyclohexanes. Incidently, ethylcyclohexane and dimethylcyclohexanes are intermediaries in the isomerization of propylcyclopentane, which in our view proceeds as follows:
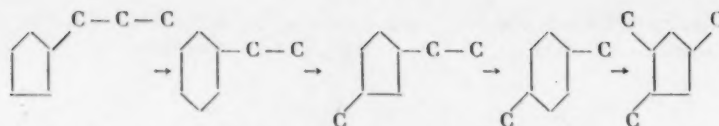
Indirect evidence of the relatively slow isomerization of ethylcyclohexane is provided by work on the isomerization of aromatic hydrocarbons in presence of platinized aluminum silicate and of hydrogen under pressure [17]. In principle, the isomerization of aromatic hydrocarbons, e.g. xylenes and ethylbenzene, in presence of multifunctional catalysts can be carried out in two stages. The hydrocarbons can first be hydrogenated to cycloalkanes at 350–380° and 25–30 atm, and then, after raising the temperature by 100–120° and lowering the pressure to 10–15 atm, we can dehydrogenate the cycloalkanes. It is clear that hydrogenation and dehydrogenation will be accompanied by isomerization reactions, as a result of which aromatic hydrocarbons will be formed which are isomers of the original hydrocarbons. It was found that the isomerization of xylenes can be effected satisfactorily in a single passage over the catalyst at 470° and 15 atm. Under these conditions, apart from 2–3% of cycloalkanes, an almost equilibrium mixture of xylenes is formed. The isomerization of aromatic hydrocarbons probably proceeds through the following stages: hydrogenation with formation of the corresponding cyclohexane homologs, isomerization of these, and dehydrogenation of the isomeric cyclohexanes into aromatic hydrocarbons:
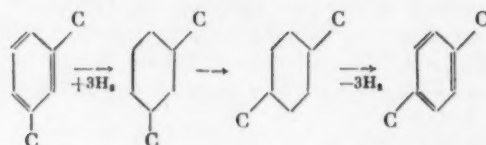
In the case of ethylbenzene and cumene the amount of cyclohexanes present in the equilibrium mixture was low and was found to be insufficient to bring about isomerization. The explanation of this should probably be sought in the slower isomerization of monosubstituted cycloalkanes already referred to. Satisfactory results on the isomerization of ethylbenzene and cumene were obtained only after preliminary hydrogenation: by 30% in the case of ethylbenzene and by 100% in the case of cumene (moreover the complete hydrogenation of cumene enabled us largely to avoid the cracking of this hydrocarbon). It is interesting to note that the composition of the aromatic hydrocarbons [17] obtained in the isomerization was (with respect to the relative contents of the various structural forms) fairly close to that of the C_8-C_9 alkylcyclohexanes in our experiments on the isomerization of cycloalkanes.

SUMMARY

1. The isomerization of C_6-C_9 cycloalkanes was carried out in presence of a multifunctional catalyst and of hydrogen under pressure.

2. The compositions of the isomerization products from C_7 and C_8 cycloalkanes were in good agreement with the calculated thermodynamic values.

3. A mechanism was proposed for the isomerization of cycloalkanes. It is considered that, as in the case of the isomerization of paraffins, the first stage of the reaction is the formation of unsaturated hydrocarbons.

4. The effects of pressure and temperature on the course of the reactions of cycloalkanes in presence of multifunctional catalysts were demonstrated.

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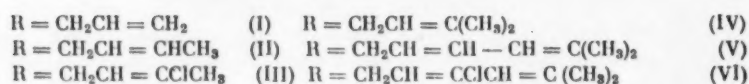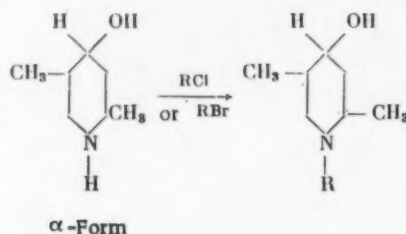** In Russian.

HETEROCYCLIC COMPOUNDS

COMMUNICATION 60. SYNTHETIC ANESTHETICS

XXI SYNTHESIS OF ESTERS OF THE α-FORMS OF 1-ALKENYL-2,5-DIMETHYL-4-PIPERIDINOLS

I. N. Nazarov, A. Sh. Sharifkanov, and K. F. Danilova

In the previous communication [1] we described benzoic esters of secondary 2,5-dimethyl- and 1,2,5-tri-methyl-4-piperidinols, which were found to have considerable anesthetic activity. In the present investigation we synthesized some new esters of the α-forms of secondary 1-alkenyl-2,5-dimethyl-4-piperidinols with the object of determining the effects of an unsaturated group attached to the nitrogen and of the influence of the acyl group on the physiological activities of these compounds.

The original 1-alkenyl (or alkadienyl)-2,5-dimethyl-4-piperidinols (I-VI) were prepared in high yield (more than 80%) by heating the corresponding 2-alkenyl halides with two moleculer proportions of the α-form of the 2,5-dimethyl-4-piperidinol [2] in benzene or dioxane solution:

α-Form

$R = CH_2CH = CH_2$ (I) $R = CH_2CH = C(CH_3)_2$ (IV)
$R = CH_2CH = CHCH_3$ (II) $R = CH_2CH = CH — CH = C(CH_3)_2$ (V)
$R = CH_2CH = CClCH_3$ (III) $R = CH_2CH = CClCH = C(CH_3)_2$ (VI)

The second molecule of 2,5-dimethyl-4-piperidinol taken was used in the binding of the hydrogen halide formed and was recovered afterwards, as in the similar alkylation of 2,5-dimethylpiperidone, described previously [3, 4].

TABLE 1

Ester	R	R'	Ester	R	R'
VII	$CH_2CH=CH_3$	C_6H_5	XIV	$CH_3CH=CHCH_3$	CH_3
VIII	$CH_2CH=CH_3$	$C_6H_5CH_3$	XV	$CH_2CH=C(CH_3)_2$	C_6H_5
IX	$CH_2CH=CH_2$	$C_6H_5OCH_2$	XVI	$CH_2CH=C(CH_3)_2$	$C_6H_5CH_3$
X	$CH_2CH=CH_2$	$C_6H_5CH=CH$	XVII	$CH_2CH=C(CH_3)_2$	$C_6H_5CH=CH$
XI	$CH_2CH=CH_2$	$C_6H_5CH_2CH_3$	XVIII	$CH_2CH=CH—CH=C(CH_3)_2$	C_6H_5
XII	$CH_2CH=CHCH_3$	C_6H_5	XIX	$CH_2CH=CClCH=C(CH_3)_2$	C_6H_5
XIII	$CH_2CH=CHCH_3$	C_5H_6			

TABLE 2
Results of Pharmacological Tests on the Esters

Compound tested	Concentration (%)				Minimum fatal dose (mg/g)
	0.25	0.5	1	2	
	Anesthesia Index				
Novocaine	109	181	255	309	0.3
Cocaine	158	401	573	730	0.15
Tetracaine	1182	1194	1289	1300	—
(VII) H OCOC₂H₅ / CH₃– –CH₃ / N / CH₃CH–CH₃	702	879	1015	1154	0.8
(IX) H OCOCH₂OC₂H₅ / CH₃– –CH₃ / N / CH₃CH–CH₃	204	294	197	653	3
(XI) H OCOCH₂CH₂C₂H₅ / CH₃– –CH₃ / N / CH₃CH–CH₃	156	—	—	242	0.8
(XII) H OCOC₂H₅ / CH₃– –CH₃ / N / CH₃CH–CHCH₃	504	961	1099	1149	0.8
(XV) H OCOC₂H₅ / CH₃– –CH₃ / N / CH₃CH–C(CH₃)₂	954	1008	1138	1285	0.5
(XVI) H OCOCH₂C₂H₅ / CH₃– –CH₃ / N / CH₃CH–C(CH₃)₂	477	866	980	1184	0.5
(XVIII) H OCOC₂H₅ / CH₃– –CH₃ / N / CH₃CH–CH–CH–C(CH₃)₂	618	979	1100	1160	1.0

The esterification of the resulting 1-alkenyl-(or alkadienyl)-2,5-dimethyl-4-piperidinols (I-VI) with acid chlorides gave the corresponding esters(VII-XIX), which are listed in Table 1:
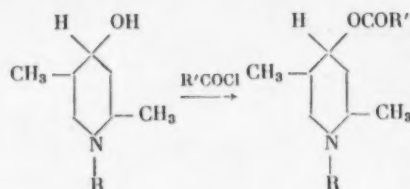
Of the thirteen esters of α-forms of 1-alkenyl-2,5-dimethyl-4-piperidinols obtained, nine (VII, IX, XI-XVI, XVIII) were tested in the form of hydrochlorides for surface anesthesia by the Renier method in the Pharmacological Laboratory of the V. M. Molotov State Medical Institute (Director of Department, Prof. I. I. Sivertsev), Kazan. The estimation of the anesthetizing effects of the esters was carried out with novocaine, cocaine, and tetracaine as standards for comparison.

Parallel tests on the esters (XII, XV, and XVIII) were carried out in Prof. M. D. Mashkovskii's laboratory (VNIKhFI), and their activity indices in 1% solution were found to be 778, 741, and 367, respectively. At 2% concentration the esters (XII and XV) cause slight irritation of the cornea of the eye. The propionic and acetic esters of 1-(2-butenyl)-2,5-dimethyl-4-piperidinol (XIII and XIV) have a very weak anesthetic effect, but all the other esters have considerable activity with comparatively low toxicity. The results of the tests are given in Table 2.

EXPERIMENTAL *

All the piperidinols and their esters synthesized in the course of this investigation corresponded to the α-isomer of 2,5-dimethyl-4-piperidinol, m.p. 96-97°, described previously [1, 2].

1- Allyl-2,5-dimethyl-4-piperidinol (I). A solution of 11.5 g of allyl chloride (b.p.43-44°) in 20 ml of dry dioxane was added dropwise to a stirred solution of 25.8 g of the α-form of 2,5-dimethyl-4-piperidinol (m.p. 96-97°) in 180 ml of dioxane contained in a round-bottomed flask fitted with mechanical stirrer, reflux condenser protected by a calcium chloride tube, and a dropping funnel. The reaction mixture was then heated in a water bath at 55-60° for 25 hours. The precipitated hydrochloride of the original piperidinol (16.3 g) was filtered off (m.p. 219°); dioxane and excess of allyl chloride were distilled off, and the residue was dissolved in dry ether; traces of hydrochloride that separated were removed. Ether was distilled off, and vacuum distillation of the residue gave 13.7 g (about 81%) of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol (I) as a viscous liquid, b.p. 109-110° (7 mm).

Found %: N 8.16; 7.97 $C_{10}H_{19}ON$. Calculated %: N 8.28.

When left in a vacuum desiccator, the piperidinol solidified in the form of readily melting crystals.

The hydrochloride was prepared by passage of dry hydrogen chloride through an alcoholic solution of the piperidinol and precipitation with dry ether; m.p. 215-216° (from alcohol).

Found %: N 7.26; 7.28; Cl 17.06; 16.73 $C_{10}H_{20}ONCl$. Calculated %: N 6.81; Cl 17.23.

In admixture with the hydrochloride of the original piperidinol (m.p. 223°) it melted at 185-187°.

1-(2-Butenyl)-2,5-dimethyl-4-piperidinol (II). A solution of 4 g of 1-bromo-2-butene (b p. 103-104° (696 mm); n_D^{20} 1.4805 [5]) in 20 ml of dry benzene was added dropwise at 50° to a stirred solution of 6.45 g of the α-form of 2,5-dimethyl-4-piperidinol in 100 ml of dry benzene. The mixture was heated at 55-60° for one hour and then left overnight. The precipitated hydrobromide of the original piperidinol was filtered off (5 g), benzene was distilled off, and the residue was vacuum-distilled, when 4 g (87%) of the α-form of 1-(2-butenyl)-

-2,5-dimethyl-4-piperidinol (II) was obtained in the form of a viscous, rapidly solidifying liquid of b.p. 108-110° (8 mm). After two crystallizations from gasoline this piperidinol melted at 91-92°.

Found %: N 7.69; 7.67 $C_{11}H_{21}ON$. Calculated %: N 7.64.

The hydrochloride melted at 196-197°.

Found %: Cl 16.58; 16.55 $C_{11}H_{22}ONCl$. Calculated %: Cl 16.17.

The picrate formed yellow, glistening needles, m.p. 147-148° (from alcohol).

Found %: N 13.59; 13.57 $C_{17}H_{24}O_8N_4$. Calculated %: N 13.58.

1-(3-Chloro-2-butenyl)-2,5-dimethyl-4-piperidinol (III). A solution of 3.2 g of 1,3-dichloro-2-butene (b.p. 123-126°; $n^{20}D$ 1.4720) [6] in 20 ml of dry benzene was added dropwise over a period of 20 minutes at 60° to a stirred solution of 6.5 g of the α-form of 2,5-dimethyl-4-piperidinol in 130 ml of dry benzene. The mixture was heated at 70-80° for two hours and then left overnight. On the next day the precipitated hydrochloride of the original piperidinol was filtered off (3.95 g), benzene was distilled off, and the residue was vacuum-distilled. This gave 4.4 g (80%) of the α-form of 1-(3-chloro-2-butenyl)-2,5-dimethyl-4-piperidinol (III) as a viscous liquid, b.p. 112-114° (2 mm); it solidified after a time, and after two crystallizations from gasoline it melted at 72.5-74°.

Found %: N 6.43; 6.34; Cl 16.10; 16.25 $C_{11}H_{20}ONCl$. Calculated %: N 6.43 Cl 16.31.

The picrate melted at 125-127°.

Found %: N 12.66; 12.53 $C_{17}H_{23}O_8N_4Cl$. Calculated %: N 12.54.

2,5-Dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (IV). A solution of 4.1 g of 1-chloro-3-methyl-2--butene (b.p. 67-68° (162 mm); $n^{20}D$ 1.4470) [7] in 10 ml of dry benzene was added dropwise to a solution of 7.75 g of the α-form of 2,5-dimethyl-4-piperidinol in 150 ml of dry benzene. The mixture was heated at 70-75° for ten hours, and the precipitated hydrochloride of the original piperidinol was then filtered off (5.1 g). The crystalline residue that remained after the removal of benzene and excess of the chloro compound under reduced pressure was crystallized from gasoline, and 4.6 g (80%) of the α-form of 2,5-dimethyl-1-(3-methyl--2-butenyl)-4-piperidinol (IV), m.p. 80-81°, was obtained.

Found %: N 7.27; 7.30 $C_{12}H_{23}ON$. Calculated %: N 7.10.

The hydrochloride melted at 192-192.5° (from a mixture of alcohol and ether).

Found %: N 6.20; 6.21; Cl 14.93; 14.97 $C_{12}H_{24}ONCl$. Calculated %: N 5.99 Cl 15.16.

The picrate formed yellow needles, m.p. 151-152° (from alcohol).

Found %: N 13.03; 12.96 $C_{18}H_{26}O_8N_4$. Calculated %: N 13.14.

2,5-Dimethyl-1-(5-methyl-2,4-hexadienyl)-4-piperidinol (V). A solution of 2.4 g of 1-chloro-5-methyl--2,4-hexadiene (b.p. 63-75° (11 mm); $n^{20}D$ 1.5090) [8] in 10 ml of dry benzene was added dropwise to the hot solution obtained by heating 3.9 g of the α-form of 2,5-dimethyl-4-piperidinol with 60 ml of dry benzene in a water bath. The mixture was heated at 70-75° for four hours and then left overnight. The precipitated hydrochloride was filtered off, benzene was distilled off under reduced pressure, and the residue was dissolved in dry ether in order to remove the hydrochloride completely. After removal of ether vacuum distillation of the reaction product gave 2 g (60%) of the α-form of 2,5-dimethyl-1-(5-methyl-2,4-hexadienyl)-4-piperidinol (V) as a viscous liquid, b.p. 136-138° (1 mm) and $n^{20}D$ 1.5230. The product solidified after a time; after crystallization from gasoline it melted at 83-84°.

Found %: N 6.24; 6.05 $C_{14}H_{25}ON$. Calculated %: N 6.26.

The picrate melted at 188-189°.

Found % N 12.33; 12.45 $C_{20}H_{28}O_8N_4$. Calculated %: N 12.36.

1-(3-Chloro-5-methyl-2,4-hexadienyl)-2,5-dimethyl-4-piperidinol (VI). A solution of 4.5 g of 1,3--dichloro-5-methyl-2,4-hexadiene (b.p. 70° (8 mm); $n^{20}D$ 1.5080) [9] in 10 ml of dry dioxane was added to

a solution of 6.5 g of the α-form of 2,5-dimethyl-4-piperidinol in 140 ml of dry dioxane. The reaction mixture was heated in a boiling-water bath for eight hours. The precipitated hydrochloride of the original piperidinol was filtered off, dioxane was distilled off under reduced pressure, and the residue was dissolved in water, acidified, and treated with ether (to remove excess of the dichloro compound). The acidic aqueous solution was saturated with potassium carbonate, and the base liberated was extracted with ether, dried with potassium carbonate, and vacuum-distilled. This gave 5.15 g (73%) of the α-form of 1-(3-chloro-5-methyl-2,4-hexadienyl)-2,5-dimethyl-4-piperidinol (VI) as a viscous liquid, b.p. 146-149° (0.05 mm) and $n^{20}D$ 1.5190.

Found %: N 5.47; 5.44 $C_{14}H_{24}ONCl$. Calculated %: N 5.43.

Benzoic Ester of 1-Allyl-2,5-dimethyl-4-piperidinol (VII). Benzoyl chloride (2.9 g) was added to a solution of 3.4 g of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol (b.p. 109-110° (7 mm)) in 10 ml of dry pyridine, and the mixture was heated at 95-105° for three hours. The mixture was cooled, a further 2.9 g of benzoyl chloride was added, and the mixture was heated at 95-105° for two hours. The precipitate that had formed was filtered off and washed with pyridine and then with ether. Three crystallizations from a mixture of absolute alcohol and ether gave 3.1 g (about 50%) of the pure hydrochloride of the benzoic ester of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol, m.p. 219-220°.

Found %: N 4.27; 4.16; Cl 11.36; 11.46 $C_{17}H_{24}O_2NCl$. Calculated %: N 4.52; Cl 11.44.

Treatment of this hydrochloride with sodium carbonate gave the free base of the benzoic ester (VII) in the form of a viscous liquid; b.p. 161-164° (2.5 mm); $n^{20}D$ 1.5200; d^{20}_4 1.0348; found MR 80.31; calculated MR 80.03.

Found %: N 4.92; 4.86 $C_{17}H_{23}O_2N$. Calculated %: N 5.12.

Phenylacetic Ester of 1-Allyl-2,5-dimethyl-4-piperidinol (VIII). A mixture of 1.7 g of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol, 2 g of phenylacetylchloride, 10 ml of dry benzene, and 0.12 g of magnesium turnings was heated at 90° for ten hours . The magnesium was separated, and the reaction product was converted into the base and extracted with ether. Vacuum distillation gave 1.28 g of the phenylacetic ester of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol as a viscous liquid; b.p. 157-158° (2 mm); $n^{20}D$ 1.5110; d^{20}_4 1.0089; found MR 85.34; calculated MR 84.65.

Found %: N 4.99; 5.14 $C_{18}H_{25}O_2N$. Calculated %: N 4.87.

The hydrochloride melted at 157-158° (from a mixture of alcohol and ether).

Found %: N 4.39; 4.06; Cl 10.64; 10.73 $C_{18}H_{26}O_2NCl$. Calculated %: N 4.33; Cl 10.95.

Phenoxyacetic Ester of 1-Allyl-2,5-dimethyl-4-piperidinol (IX). A mixture of 3.38 g of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol, 3.78 g of phenoxyacetyl chloride, 20 ml of dry benzene, and 0.24 g of magnesium turnings was heated at 90° for nine hours. The precipitate formed was filtered off. Crystallization from a mixture of absolute alcohol and ether gave 4.05 g (about 60%) of the hydrochloride of the phenoxyacetic ester of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol, m.p. 184-185.

Found % : N 4.10; 4.48; Cl 10.91; 10.79 $C_{18}H_{26}O_3NCl$. Calculated % : N 4.12; Cl 10.45.

Cinnamic Ester of 1-Allyl-2,5-dimethyl-4-piperidinol (X). A mixture of 1.69 g of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol, 4.17 g of cinnamoyl chloride, and 10 ml of dry pyridine was heated at 95-105° for six hours. The reaction product was precipitated with dry ether, and crystallization from a mixture of alcohol and ether and then from benzene gave 2.7 g of the hydrochloride of the cinnamic ester of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol, m.p. 195-197°.

Found %: N 4.29; 4.22; Cl 10.95; 10.74 $C_{19}H_{26}O_2NCl$. Calculated %: N 4.17; Cl 10.56.

Hydrocinnamic Ester of 1-Allyl-2,5-dimethyl-4-piperidinol (XI). A mixture of 1.7 g of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol, 3.4 g of hydrocinnamoyl chloride, 10 ml of dry benzene, and 0.12 g of magnesium turnings was heated at 90-95° for ten hours. The magnesium was separated, benzene was distilled off, and the reaction product was treated with sodium carbonate solution and extracted with ether. Vacuum distillation gave 2 g of the hydrocinnamic ester of the α-form of 1-allyl-2,5-dimethyl-4-piperidinol as a viscous liquid; b.p. 166-169° (2 mm); $n^{20}D$ 1.5145; d^{20}_4 1.0140; found MR 89.56; calculated MR 89.27.

Found %: N 4.78; 4.57 $C_{19}H_{27}O_2N$. Calculated %: N 4.65.

The hydrochloride melted at 118-120° (from benzene).

Found %: N 4.11; 4.19; Cl 10.91; 11.00 $C_{19}H_{28}O_2NCl$. Calculated %: N 4.15; Cl 10.52.

Benzoic Ester of 1-(2-Butenyl)-2,5-dimethyl-4-piperidinol (XII). Benzoyl chloride (5 g) was added to a solution of 4.6 g of the α-form of 1-(2-butenyl)-2,5-dimethyl-4-piperidinol (m.p. 91°) in 15 ml of pyridine. The reaction mixture was heated at 100-110° for two hours. On the next day,pyridine and excess of the acid chloride were distilled off under reduced pressure, the residue was dissolved in water, and the aqueous solution was then treated with ether and saturated with sodium carbonate; the liberated base was extracted with ether. Vacuum distillation gave 5.9 g (about 82 %) of the benzoic ester of the α-form of 1-(2-butenyl)-2,5-dimethyl- -4-piperidinol as a viscous liquid; b.p. 140-145° (1 mm); $n^{20}D$ 1.5195; d^{20}_4 1.027; found MR 84.01; calculated MR 84.65.

The base was converted into its hydrochloride, which was obtained in the form of glistening needles, m.p. 116-118°, after crystallization from a mixture of alcohol and ether.

Found %: N 4.55; 4.42; Cl 10.47; 10.61 $C_{19}H_{26}O_2NCl$. Calculated %: N 4.32; Cl 10.98.

Propionic Ester of 1-(2-Butenyl)-2,5-dimethyl-4-piperidinol (XIII). A mixture of 5.5 g of the α-form of 1-(2-butenyl)-2,5-dimethyl-4-piperidinol (m.p. 90-91°), 3.37 g of propionyl chloride, and 15 ml of dry pyridine was heated at 80° for 2.5 hours. After the usual treatment of the reaction product, vacuum distillation of the liberated base gave 1.5 g of the propionic ester of the α-form of 1-(2-butenyl)-2,5-dimethyl-4-piperidinol; b.p.113° (3 mm); $n^{20}D$ 1.4678; d^{20}_4 0.968; found MR 69.20; calculated MR 69.77.

Found %: N 5.64; 5.90 $C_{14}H_{25}O_2N$. Calculated %: N 5.58.

The hydrochloride melted at 204-205° (from a mixture of alcohol and ether).

Found %: Cl 13.37; 13.30 $C_{14}H_{26}O_2NCl$. Calculated %: Cl 12.89.

Acetic Ester of 1-(2-Butenyl)-2,5-dimethyl-4-piperidinol (XIV). A mixture of 1.9 g of the α-form of 1-(2-butenyl)-2,5-dimethyl-4-piperidinol (m.p. 90-91°), 11 g of freshly distilled acetic anhydride, and one drop of concentrated sulfuric acid was heated in a boiling water bath for six hours. After the usual treatment, vacuum distillation of the liberated base gave 1.8 g (75 %) of the acetic ester of the α-form of 1-(2-butenyl)- -2,5-dimethyl-4-piperidinol; b.p.88-89° (1.5 mm); $n^{20}D$ 1.4660; d^{20}_4 0.9608; found MR 65.65; calculated MR 65.15.

Found %: N 6.29; 6.37 $C_{13}H_{23}O_2N$. Calculated %: N 6.22.

The hydrochloride melted at 199-200° (from absolute alcohol).

Found %: Cl 13.97; 14.08 $C_{13}H_{24}O_2NCl$. Calculated %: Cl 13.57.

Benzoic Ester of 2,5-Dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (XV). A mixture of 1.97 g of the α-form of 2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (m.p. 80-81°), 10 ml of dry pyridine, and 2.23 g of benzoyl chloride was heated in a boiling water bath for 90 minutes. The mixture was cooled, a further 2 g of benzoyl chloride was added, and the mixture was again heated at 95-105° for two hours. On the next day the reaction product was precipitated with dry ether, filtered off, washed with ether, and crystallized twice from benzene. This gave 2.53 g (about 75 %) of the pure hydrochloride of the benzoic ester of the α-form of 2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol, m.p. 182-183°.

Found %: N 4.35; 4.47; Cl 10.51; 10.77 $C_{19}H_{28}O_2NCl$. Calculated %: N 4.15; Cl 10.49.

Treatment of this hydrochloride with sodium carbonate gave the free base of the benzoic ester as a viscous liquid, b.p. 169° (2 mm) and $n^{20}D$ 1.5210.

Found %: N 4.75; 4.77; $C_{19}H_{27}O_2N$. Calculated %: N 4.65.

Phenylacetic Ester of 2,5-Dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (XVI). A mixture of 2.46 g of the α-form of 2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (m.p. 80-81°), 25 ml of benzene, and 2.5 g of phenylacetyl chloride was heated in presence of 0.15 g of magnesium turnings at 85-90° for five hours.

The precipitate formed was filtered off, and was washed with benzene and then ether. Three crystallizations from benzene gave 2.3 g of the pure hydrochloride of the phenylacetic ester of 2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol, m.p. 148-150°.

Found %: N 4.07; 4.27; Cl 10.50; 10.53 $C_{20}H_{30}O_2NCl$. Calculated %: N 3.98; Cl 10.09.

The free base of the phenylacetic ester is a viscous liquid, b.p. 181-184° (2 mm) and $n^{20}D$ 1.5123.

Found %: N 4.56; 4.59 $C_{20}H_{29}O_2N$. Calculated %: N 4.44.

Cinnamic Ester of 2,5-Dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (XVII). Cinnamoyl chloride (4.16 g) was added to a solution of 1.97 g of the α-form of 2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (m.p. 79-80°) in 11 ml of dry pyridine. The mixture was heated at 100-105° for six hours. The reaction product was precipitated with ether, filtered off, and washed with ether. Crystallization from benzene and then from a mixture of alcohol and ether gave 2.9 g of the pure hydrochloride of the cinnamic ester of the α-form of 2,5--dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol, m.p. 146-147°.

Found %: N 3.91; 3.97; Cl 9.77; 10.06 $C_{21}H_{30}O_2NCl$. Calculated %: N 3.85; Cl 9.76.

The free base of the cinnamic ester is a viscous liquid, b.p. 205-207° (2 mm).

Found %: N 4.83; 4.85 $C_{21}H_{29}O_2N$. Calculated %: N 4.28.

Benzoic Ester of 2,5-Dimethyl-1-(5-methyl-2,4-hexadienyl)-4-piperidinol (XVIII). Benzoyl chloride (3.7 g) was added to a solution of 3.55 g of the α- form of 2,5-dimethyl-1-(5-methyl-2,4-hexadienyl)-4-piperidinol (m.p. 83-84°) in 10 ml of dry pyridine. The mixture was heated at 110-120° for three hours. Pyridine and excess of the acid chloride were distilled off under reduced pressure; the residue was dissolved in water, the solution was treated with ether and then with sodium carbonate, and the base liberated was extracted with ether. Ether was distilled off, and the solid residue was crystallized twice from gasoline; this gave 2.5 g (50 %) of the benzoic ester of the α-form of 2,5-dimethyl-1-(5-methyl-2,4-hexadienyl)-4-piperidinol, m.p. 59-60°.

Found %: N 4.30; 4.24 $C_{21}H_{29}O_2N$. Calculated %: N 4.33.

The hydrochloride melted at 173-174° (from alcohol).

Found %: Cl 9.88; 10.02 $C_{21}H_{30}O_2NCl$. Calculated %: Cl 9.76.

Benzoic Ester of 1-(3-Chloro-5-methyl-2,4-hexadienyl)-2,5-dimethyl-4-piperidinol (XIX). A mixture of 3.25 g of the α-form of 1-(3-chloro-5-methyl-2,4-hexadienyl)-2,5-dimethyl-4-piperidinol, 2.6 g of benzoyl chloride, and 15 ml of pyridine was heated in a boiling water bath for five hours. The usual treatment of the reaction product and vacuum distillation gave 1.7 g of the benzoic ester of the α-form of 1-(3-chloro-5-methyl--2,4-hexadienyl)-2,5- dimethyl-4-piperidinol, b.p. 170-180° (0.5 mm) and $n^{20}D$ 1.5280 .

Found %: N 3.85; 4.14 $C_{21}H_{28}O_2NCl$. Calculated %: N 3.87.

The hydrochloride of this benzoic ester was a noncrystallizing oil.

SUMMARY

1. Reaction of the α-form of 2,5-dimethyl-4-piperidinol with halogen compounds of the allyl halide type gave the corresponding 1-alkenyl(or alkadienyl)-2,5-dimethyl-4-piperidinols (I-VI) in high yield (more than 80 %).

2. Esterification of the piperidinols (I-VI) with acid chlorides gave the esters (VII-XIX), which were sub - jected to pharmacological tests for surface anesthesia. Of the compounds tested, the propionic and acetic esters of 1-(2-butenyl)-2,5-dimethyl-4-piperidinol (XIII) and (XIV) showed very feeble activity, but all the other esters have high anesthetic activity with comparatively low toxicity.

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*Original Russian pagination. See C. B. Translation.

N-OXIDES OF SOME HETEROCYCLIC BASES

COMMUNICATION 1. PREPARATION AND PROPERTIES OF N-OXIDES OF NICOTINE

Ia. L. Gol'dfarb and V. K. Zvorykina

As a tertiary-tertiary diacid base, nicotine can, on oxidation, give oxides of three types:

(I)
Nicotine
N-oxide

(II)
Nicotine
N'-oxide

(III)
Nicotine
N,N'-dioxide
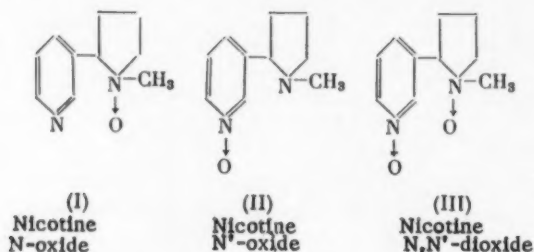
Investigation of the oxidation of nicotine began already at the end of last century, but it was concerned almost exclusively with compounds of the first type. In 1891 Pinner and Wolffenstein [1] oxidized nicotine with hydrogen peroxide and isolated a compound $C_{10}H_{14}N_2O$, which was free from carbonyl and alcohol groups and which they called "oxynicotine". In the study of the properties of oxynicotine they obtained two compounds of the same elementary composition, one containing carbonyl and the other noncarbonyl oxygen. The authors proposed the following scheme for their formation:
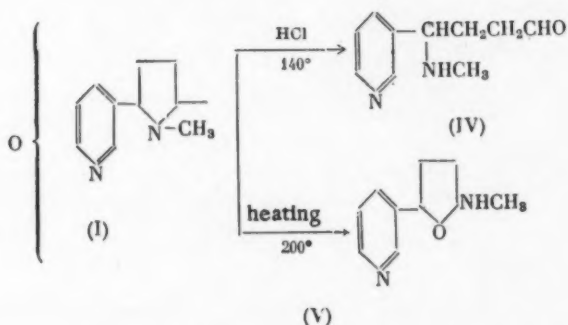
With regard to oxynicotine (I), Pinner suggested that it was a "polymer" of an aldehyde, because it gave no reactions for the carbonyl group, but was converted into an aldehyde ("pseudooxynicotine" (IV))when heated with acid. Somewhat later (1901), Auerbach and Wolffenstein [2], on the basis of their work on the oxidation of 1-methylpiperidine with hydrogen peroxide, established the correct structure of oxynicotine and proposed an N-oxide formula with the oxygen attached to the pyrrolidine nitrogen:
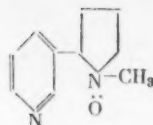
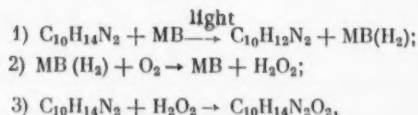The authors showed that the oxygen is readily eliminated by treatment with sulfur dioxide or nitrogen dioxide.

In a study of the action of acetic anhydride on N-oxides of alkaloids, the Polonovskis [3] obtained nor-nicotine [VI] from Pinner's oxynicotine (I); they considered that the reaction proceeds as follows:
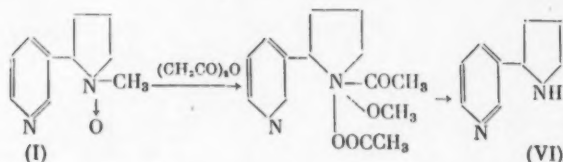
In 1948 there appeared a short paper by Weil [4] on the photochemical oxidation of nicotine in presence of Methylene blue. The author isolated a viscous yellow oil of elementary composition $C_{10}H_{14}N_2O_2$; he suggested that the oxidizing agent acted on the $> N-CH_3$ grouping of the pyrrolidine ring, for 1-methylpyrrolidine is itself readily oxidized under these conditions, whereas various 3-substituted pyridines do not undergo photochemical oxidation. Weil suggested the following scheme of reaction:

1) $C_{10}H_{14}N_2 + MB \xrightarrow{light} C_{10}H_{12}N_2 + MB(H_2)$;

2) $MB(H_2) + O_2 \rightarrow MB + H_2O_2$;

3) $C_{10}H_{14}N_2 + H_2O_2 \rightarrow C_{10}H_{14}N_2O_2$,

but gave no proof of the structure of the product, gave no constants for it, and did not characterize it by suitable derivatives. In 1950 Hains and Eisner [5] repeated Pinner's work and showed that pseudooxynicotine (IV) is not an aldehyde, as Pinner supposed, but 4-methylamino-1-(3-pyridyl)-1-butanone (VII), which was proved by confirmatory synthesis from 1-methyl-3-nicotinoyl-2-pyrrolidone:
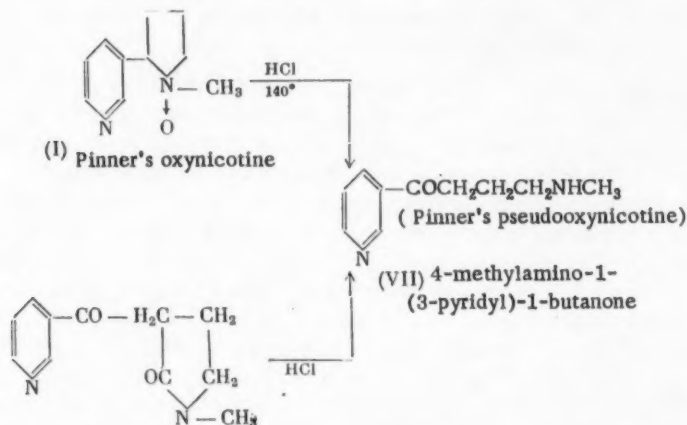
1-methyl-3-nicotinoyl-2-pyrrolidone

In the same year Reyburg and Harlan [6] determined the true structure of Pinner's "nicotone" and showed that this compound does not contain a five-membered furan ring (V), but a six-membered oxazine ring (VIII), and they confirmed this by investigation of the ultraviolet absorption spectra:

(I) "oxynicotine"   (VIII)

tetrahydro-2-methyl-
-6-(pyridyl)-2H-1,2-oxazine
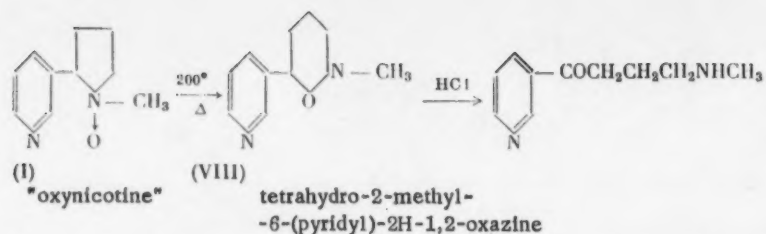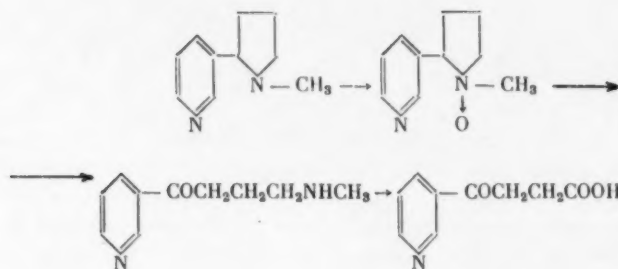
In 1954 Wada and co-workers [7] studied the cleavage of nicotine by soil bacteria and suggested the following scheme for this process, in which oxynicotine is regarded as the first intermediate product in the reaction:


In 1955 Frankenburg and co-workers [8] isolated oxynicotine and products of its further breakdown (1-
-(3-pyridyl)-1-butanone, nicotinamide, and N-methylnicotinamide) in the enzymic degradation of tobacco, and they gave a method for the isolation and quantitative determination of oxynicotine in tobacco extracts. With regard to the properties of oxynicotine, i.e.,nicotine N-oxide (I), it is reported in the literature that it can be isolated in the solid state by long standing of the oily product in a vacuum desiccator; Pinner states that it decomposes at 150°. Other authors gives no constants for the solid product. It is usual to use it in further reac-tions as an oil and to characterize it on isolation as the picrate. Various melting points have been attributed to the picrate. Pinner gives 154-158° [1], and later papers give values ranging from 167° to 175°. In work carried out in 1955 a picrate of m.p. 168° is used as a standard for comparisons [8]. Until now, nicotine N'-oxide (II) and nicotine N,N'-dioxide (III) have not been described.

In a study of the oxidation reactions of nicotine we succeeded in preparing all three possible N-oxides (I, II, and III) in a crystalline state. Nicotine N-oxide prepared under Pinner's conditions [1] was converted into its hydrochloride (m.p. 176.5-178°), and in the decomposition of this the crystalline base was isolated. After crystallization from acetone and vacuum drying at 100° we obtained colorless needles, m.p. 172-173°. The pic-rate, both when prepared from the hydrochloride and when prepared from the base, had m.p. 168°.

For the synthesis of nicotine N,N'-dioxide (III) we chose conditions described by some Japanese chemists [9]: oxidation with 30% H_2O_2 in glacial acetic acid. The dioxide was precipitated directly from the reaction product by means of acetone and was obtained as a compound with one molecule of H_2O_2. After purification through the hydrochloride we obtained crystals of nicotine N,N'-dioxide containing two molecules of water;m.p. 78°,after vacuum drying at 100° we obtained the anhydrous base,m.p.183. The picrate,both from the base and from the hydrochloride, had m.p. 238-239° and was found to be a monopicrate. When nicotine N,N'-dioxide was treated with an alcoholic solution of sulfur dioxide, elimination of one atom of oxygen occurred with formation of nicotine N'-oxide (II). We succeeded in distilling this compound under reduced pressure; after crystallization from a mixture of diethyl ether and petroleum ether we obtained crystals of m.p. 52°.

Apart from nicotine N'-oxide, by precipitation with acetone the reaction product yielded a second com-pound, which contained sulfur and corresponded in analysis to a monosulfate of the monoxide containing one molecule of acetone. There are indications in the literature of the possibility of the formation of such acetone compounds from N-oxides [10]

$$-O \quad CH_3$$
$$\quad \diagdown C \diagup$$
$$-O \quad CH_3$$
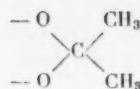
Its structure has not yet been finally established. When nicotine N,N'-dioxide (III) and nicotine N'-dioxide (II) were reduced with zinc in an acid medium, in both cases the product was nicotine:
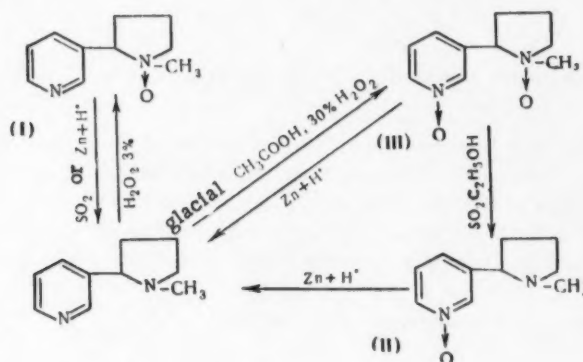
The structures of the N-oxides that we synthesized can, as will be seen from the scheme, be assigned on the basis of their properties and methods of preparation. It is known [11] that treatment of N-oxides of aliphatic amines and hydrogenated heterocyclic amines with sulfur dioxide readily eliminates the N-oxygen, whereas in aromatic systems the N-oxide linkage is preserved. Hence the elimination of one oxygen of the dioxide (III) by treatment with sulfur dioxide in alcoholic solution confirms the presence of an N-oxide link in the pyrrolidine ring. The conversion of the dioxide (III) into the monoxide (II), which is distinct from Pinner's oxynicotine (I), proves the presence of oxygen in the pyridine ring. The formation of nicotine by the reduction of both the dioxide (III) and the monoxide (II) provides proof of the presence of unopened pyridine and pyrrolidine rings in the oxidation products (III) and (II). A further argument is provided by the pH values, which we determined for all three N-oxide bases; this gives a clear picture of rising basic character from the weakly acid, almost neutral N,N'-dioxide (III) to the strongly alkaline N'-oxide (II):

(III) pH 6.5 — 7   (I) pH 7.5   (II) pH ~ 9
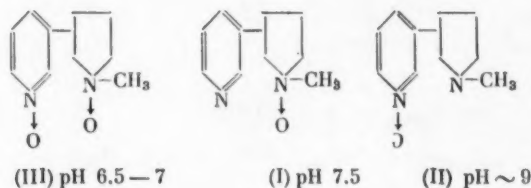
EXPERIMENTAL

Preparation of the Dihydrochloride of Nicotine N-Oxide [1]. The oxidation was carried out with 3% H_2O_2 under the conditions described by Pinner. The oil (10 g) remaining after removal of solvent under reduced pressure, was treated with alcohol saturated with HCl and with dry ether. The hydrochloride, which was at first precipitated as an oil, solidified after two days. The precipitate was fairly hygroscopic; it was filtered off rapidly, washed with a little alcohol and dry ether, and vacuum-dried at 70°; m.p. of hydrochloride 176.5-178° (with decomposition); yield 11.5 g (81%).

Found %: Cl 28.68; 28.24 $C_{10}H_{16}N_2Cl_2O$. Calculated %: Cl 28.29.

The picrate prepared from the hydrochloride had m.p. 168° [8].

Isolation of Nicotine N-Oxide Base from the Hydrochloride. The hydrochloride (3 g) was dissolved in 15 ml of water, and the solution was saturated with potassium carbonate. The layer of pale-yellow oil that formed on the surface was separated, the solution was extracted with isobutyl alcohol, and the extracts were combined with the oil and dried with potassium carbonate. Isobutyl alcohol was distilled off under reduced pressure, and the residue was crystallized from acetone and vacuum-dried at 100°. This gave 1.57 g (74%) of nicotine N-oxide base, m.p. 172-173° (in a sealed capillary). The pure base crystallizes in long colorless crystals, is odorless, and deliquesces very slowly in the air.

Found %: C 67.48; 67.31; H 7.95; 7.90; N 15.75; 15.81 $C_{10}H_{14}N_2O$. Calculated %: C 67.36; H 8.00; N 15.69.

The picrate prepared from the base melted at 168°; the pH of nicotine N-oxide was 7.5 (determined by Michaelis's method in 0.01 N solution).

Preparation of Nicotine N,N'-Dioxide. Nicotine (50 g) was added gradually to a mixture of 200 ml of 30% H_2O_2 and 1200 ml of glacial acetic acid. The resulting solution was heated for 20 hours at 65-70°. Acetic acid was distilled off at 40-50° under reduced pressure, and the residue was treated with absolute alcohol and benzene with subsequent removal of solvent under reduced pressure. This operation was repeated three times. A clear yellow oil remained. A small sample yielded a picrate of m.p. 230-233°. A mixture of this with nicotine picrate (m.p. 218-219°) melted at 202-204°. The oil was dissolved in absolute methanol and precipitated with acetone, and a little amorphous yellow material was isolated; it had no definite melting point and gradually decomposed in the range 80-140°. For analysis the product was vacuum-dried to constant weight at 40-50° (4 mm); its elementary composition corresponded to the formula $C_{10}H_{16}N_2O_3$, which corresponds closely to nicotine dioxide in combination with one molecule of H_2O_2. This compound liberates iodine from acidic KI solution.

Found %: C 53.72; 53.63; H 6.61; 6.65; N 11.64; 11.65 $C_{10}H_{16}N_2O_3$. Calculated %: C 52.63; H 7.01; N 12.28.

Isolation of Nicotine N,N'-Dioxide as the Dihydrochloride. The oil obtained in the above-described experiment was dissolved in 150 ml of absolute ethanol and precipitated with alcohol saturated with HCl. The precipitate was filtered off, washed with a little absolute alcohol and ether and dried in a vacuum desiccator. This gave 28.7 g of a substance of m.p. 187-188° (Fraction I). Precipitation of the filtrate with dry ether gave a further 27.5 g of hydrochloride (Fraction II), m.p. 183-185°. With further addition of ether a mixture of oil and crystals was precipitated, and from this it was possible to obtain some more of the hydrochloride (Fraction III), m.p. 180-182°. Recrystallization of Fractions II and III from alcohol raised their melting points to 188°. The yield of dihydrochloride was 70-75%.

The picrate prepared from the hydrochloride of m.p. 188° had m.p. 239-240°, and a mixture of it with the picrate obtained from the original oil (m.p. 233°) had m.p. 237-238°. From the mother liquor remaining after the separation of Fraction III of hydrochloride crystals we obtained two picrates, m.p. 230-232° and 166-167°. The latter picrate was that derived from nicotine N-oxide. In admixture with a pure sample (m.p. 168°) it melted at 167-168°.

Analysis of hydrochloride of m.p. 188°

Found %: C 44.63; 44.87; H 6.03; 6.09; Cl 26.61; 26.31; $C_{10}H_{16}N_2Cl_2O_2$. Calculated %: C 44.94; H 6.00; Cl 26.59.

Analysis of picrate of m.p. 239-240°

Found %: C 45.35; 45.38; H 4.06; 4.08; N 16.23 $C_{16}H_{17}N_5O_9$. Calculate %: C 45.15; H 4.02; N 16.55.

Preparation of Mercury Complex of Nicotine N,N'-Dioxide. A saturated solution of $HgCl_2$ was added to an aqueous solution of the dihydrochloride. The white, crystalline precipitate of the mercury compound was recrystallized from water and dried at 75-80°. It formed long, colorless needles, m.p. 155-156°.

Found %: C 11.88; 11.95; H 1.48; 1.51 $C_{10}H_{14}N_2O_3 3HgCl_2$. Calculated %: 11.89; H 1.30.

Isolation of Nicotine N,N'Dioxide Base from the Dihydrochloride. The experiment was carried out under the same conditions as in the case of nicotine N-oxide. After removal of isobutyl alcohol and treatment with

acetone, 6.6 g (75.5%) of crystalline base was obtained from 10.3 g of the hydrochloride. After being crystallized from acetone and dried in a vacuum desiccator, the base was obtained as a crystal hydrate with two molecules of water and had m.p. 78° (colorless needles). After vacuum drying at 100° the melting point was raised to 183° (sealed capillary). The weight loss was 15.65%, which corresponds to two H_2O molecules.

Analysis of nicotine N, N'-dioxide base, m.p. 183°

Found %: C 60.97; 61.11; H 7.41; 7.32; N 14.58; 14.48 $C_{10}H_{14}N_2O_2$. Calculated %: C 61.85; H 7.21; N 14.43.

The picrate prepared from the base, both the preparation of m.p. 78° and that of m.p. 183°, melted at 238-239° and showed no depression of melting point in admixture with the picrate prepared from the hydrochloride. The pH of nicotine N, N'-dioxide was 6.5-7 (determined by Michaelis's method in 0.01 N solution).

Reduction of Nicotine N,N'-Dioxide Dihydrochloride. The dioxide hydrochloride (2 g) was reduced with zinc in 12% hydrochloric acid at 20-25°. The solution was rendered alkaline, and nicotine was extracted with ether; yield 1.16 g. A sample gave a picrate of m.p. 207-208°, raised to 218-219° by recrystallization. A mixture of this with the picrate of pure nicotine (m.p. 218-219°) melted at the same temperature.

Preparation of Nicotine N'-Oxide. Nicotine N,N'-oxide (50 g) was prepared as an oil (without further purification) under the conditions of the previous experiment and was dissolved in 200 ml of absolute ethanol; the solution was cooled with water and ice, saturated with sulfur dioxide, and left for 12 hours. The excess of sulfur dioxide was removed by purging with dry air, and alcohol was removed under reduced pressure. The residue was an oil. Repeated treatment with acetone gave 10.6 g of a yellow, amorphous substance, which contained sulfur, gave a positive reaction for SO_4^{2-} ions, and decomposed slowly when heated, with evolution of gas; its elementary composition $C_{13}H_{22}N_2SO_6$ corresponded to a compound formed from one molecule of the monoxide, one molecule of H_2SO_4, and one molecule of actone; its structure has not yet been established. For the purposes of analysis the compound was twice precipitated from absolute methanol with acetone and was vacuum-dried at 45-50°. The noncrystallizing oil remaining after the removal of acetone was converted into a picrate by fractional precipitation with picric acid. The first picrate fraction was precipitated as an oil, which rapidly solidified; m.p. 110-130°. By further addition of picric acid and by evaporation of the mother liquor we obtained picrates of m.p. 147-151° and 158-160° (62.1 g). After two crystallizations they were both found to be identical;their melting point rose to 161° and did not change further (yield 44.5 g). A mixture of this picrate with the picrate of the N-oxide (m.p. 168°) melted at 143-147°.

Analysis of the sulfur-containing product

Found %: C 46.32; 46.62; H 6.43; 6.59; S 9.35; 9.34 $C_{13}H_{22}N_2SO_6$. Calculated %: C 46.70; H 6.71; S 9.62.

Analysis of the picrate of m.p. 161°

Found %: C 41.70; 41.68; H 3.23; 3.23; N 17.52; 17.57 $C_{22}H_{20}O_{15}N_8$. Calculated %: C 41.51; H 3.19; N 17.61.

Preparation of Nicotine N'-Oxide Dihydrochloride from the Picrate. The picrate of m.p. 161° (23.5 g) was treated several times with 12% hydrochloric acid. The precipitated picric acid was filtered off, the hydrochloric acid solution was extracted with ether and the residue remaining after removal of ether was added to the precipitate (in all, 16.2 g of picric acid). The hydrochloric acid solution was vacuum-evaporated. The residue (a yellow oil) was treated several times with absolute alcohol with subsequent vacuum distillation of solvent. Dry acetone (100 ml) was added to the oily residue. On the next day the oil crystallized. We obtained 7.85 (84%) of hydrochloride, m.p. 187-188°. When it was precipitated from methanol with acetone its melting point was raised to 191-192°. A mixture with nicotine N-oxide dihydrochloride (m.p. 176.5-178°) melted at 150-160°.

Analysis of the dihydrochloride

Found %: C 47.95; 47.76; H 6.69; 6.55; N 11.31; 11.07; Cl 28.32; $C_{10}H_{16}N_2Cl_2O$. Calculated %: C 47.81; H 6.38; N 11.15; Cl 28.29.

The picrate prepared from the hydrochloride had m.p. 161°, undepressed by admixture of the original picrate. The mercury complex prepared from the hydrochloride had m.p. 175-176° (long colorless needles).

Found %: C 15.45; 15.76; H 2.36; 2.39; $C_{10}H_{14}N_2O \cdot 2HgCl_2 \cdot H_2O$. Calculated %: C 15.89; H 2.12.

Isolation of Nicotine N'-Oxide Base from the Dihydrochloride.   The experiment was carried out under the same conditions as in the case of nicotine N-oxide. The residue remaining after the distillation of isobutyl alcohol was dissolved in acetone, and a small amount of suspended matter was filtered off. Acetone was distilled off, and the residue (1 g of pale-yellow oil) was vacuum-distilled; b.p. 158-160° (1.5 mm). From 1.7 g of the hydrochloride we obtained 0.69 g of base. After being crystallized from a mixture of diethyl ether and petroleum ether and vacuum-dried at 35° it melted at 52° (colorless needles).

Found %: C 67.28; 67.43; H 8.00 7.91; N 15.61 $C_{10}H_{14}N_2O$. Calculated %: C 67.36; H 8.00; N 15.69.

Its picrate had m.p. 161°, undepressed by admixture of picrate prepared from the hydrochloride (m.p. 161°). The pH of nicotine N'-oxide base (0.01 N solution) was about 9.

Reduction of Nicotine N'-Oxide. This was carried out under the same conditions as the reduction of the dioxide. From 0.5 g we obtained 0.31 g of nicotine; m.p. of picrate 217-219°. A mixture with a pure sample (m.p. 218-219°) melted at 218-219°.

SUMMARY

1. In a study of the oxidation of nicotine with hydrogen peroxide all three possible N-oxides were prepared in the crystalline state; of these, nicotine N,N'-dioxide and nicotine N'-oxide (oxygen on the pyridine nitrogen) have not been described previously.

2. Nicotine N,N'-dioxide was prepared as a crystal hydrate with two molecules of water, and also as the anhydrous base, the monopicrate, the dihydrochloride, and the mercury complex.

3. Nicotine N'-oxide was prepared as the crystalline base, the dihydrochloride, the dipicrate, and the mercury complex.

4. From nicotine N-oxide, which was prepared previously by Pinner and is known in the literature as "oxynicotine", we obtained the previously undescribed hydrochloride and isolated the anhydrous base.

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OLIGOMERIZATION

COMMUNICATION 3. REACTION OF DIVINYL ETHER
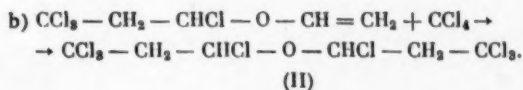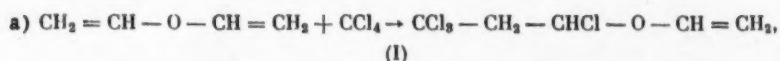## WITH CARBON TETRACHLORIDE

M. F. Shostakovskii, A. V. Bogdanova, G. I. Plotnikova,
and E. V. Dubrova

In previous communications [1,2] we described the conditions for reaction between some vinyl ethers of general formula $CH_2 = CH - OR$ with carbon tetrachloride under the influence of various reagents and agencies capable of initiating reactions proceeding by a free-radical mechanism. It was found that the behavior of vinyl ethers in this reaction is greatly affected by the alkoxy group (OR), which exhibits different reactivities in presence of different reagents capable of breaking down into free radicals. This was confirmed also for the reactions of phenyl, decahydro-2-naphthyl, and cyclohexyl vinyl ethers [3].

In the symmetrical divinyl ether the group R is vinyl, of which the effect in chemical reactions has received little study. We considered it desirable to investigate the conditions for reaction between divinyl ether and carbon tetrachloride and observe the selective behavior of the vinyl ether toward various initiators in this reaction, particularly as the behavior of divinyl ether toward peroxides is known to differ from that of alkyl vinyl ethers [4]. Relatively little work has been done on the behavior of divinyl ether in chemical reactions. Apart from the information mentioned above [4], it is known that this ether can by hydrogenated over platinum, reacts with sodium, and forms a copolymer with maleic anhydride [5]. It has been observed also that the polymerization of divinyl ether is retarded by alkaline reagents [6, 7]. Shostakovskii and Dubrova described an improved method of preparing divinyl ether from bis-2-chloroethyl ether, and also its hydrolysis and the addition of hydrogen chloride, chlorine, and bromine [8]. In this work, on the basis of the high tendency for the α-chloro and α,β-dichloro ethers obtained to undergo hydrolysis, an analogy was drawn between them and the α-chloro and α,β-dichloro dialkyl ethers studied previously [9, 10].
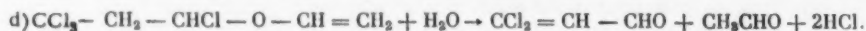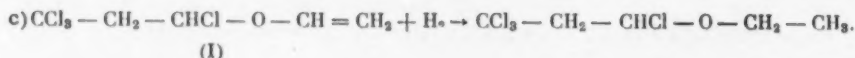
Investigation of the properties of alkyl and aryl tetrachloropropyl ethers [1, 2] showed that, owing to the mobility of α-chlorine, these compounds are again somewhat reminiscent of α-chloro ethers in their reactivity. However, the presence of three other chlorine atoms in the γ-position makes the molecule more stable under normal conditions, and all reactions in which heat must be applied inevitably result in the formation of derivatives of 3,3-dichloroacrolein. It was considered that it would be interesting also to compare the properties of the alkyl tetrachloropropyl ethers prepared by us earlier [1,2] with those of the products of the addition of carbon tetrachloride to divinyl ether.

The addition of carbon tetrachloride to divinyl ether was effected by heating these substances together in presence of various amounts of benzoyl peroxide, 2,2'-azobis [2-methylpropionitrile], and platinized charcoal, and also by ultraviolet irradiation; the relative amounts of the ether and carbon tetrachloride were varied. The reaction of divinyl ether with carbon tetrachloride proceeds in stages according to Equations (a) and (b) and yields 1,3,3,3-tetrachloropropyl vinyl ether (I) and bis-1,3,3,3-tetrachloropropyl ether (II):

$$\text{a) } CH_2 = CH - O - CH = CH_2 + CCl_4 \rightarrow CCl_3 - CH_2 - CHCl - O - CH = CH_2,$$

$$(I)$$

$$\text{b) } CCl_3 - CH_2 - CHCl - O - CH = CH_2 + CCl_4 \rightarrow$$
$$\rightarrow CCl_3 - CH_2 - CHCl - O - CHCl - CH_2 - CCl_3.$$

$$(II)$$

The proportions of the products depends on the proportions of the reactants taken, but we did not succeed in stopping the reaction to any substantial extent at the first stage. In addition to the products (I) and (II) there was a polymeric residue consisting of a mixture of products of the addition of carbon tetrachloride to divinyl ether polymers. Benzoyl peroxide and 2,2'-azobis[2-methylpropionitrile] were found to be effective initiators of this reaction. Unlike alkyl vinyl ethers, divinyl ether does not react with carbon tetrachloride under the in-fluence of platinized charcoal or ultraviolet radiation.

The structure of the tetrachloropropyl vinyl ether (I) was proved by hydrogenation and by hydrolysis, as a result of which we obtained ethyl 1,3,3,3-tetrachloropropyl ether by Equation (c) and 3,3-dichloroacrolein, acetaldehyde, and hydrogen chloride by Equation (d):

$$c) CCl_3 - CH_2 - CHCl - O - CH = CH_2 + H_\bullet \rightarrow CCl_3 - CH_2 - CHCl - O - CH_2 - CH_3.$$
$$(I)$$

$$d) CCl_3 - CH_2 - CHCl - O - CH = CH_2 + H_2O \rightarrow CCl_2 = CH - CHO + CH_3CHO + 2HCl.$$

It is interesting that the bis-tetrachloropropyl ether (II) is not hydrolyzed with water or 2% sulfuric acid at the boil; it remains unchanged under hydrolysis conditions that would be very severe for alkyl 1-chloroalkyl and alkyl tetrachloropropyl ethers. Such behavior is probably to be explained by the symmetrical structure of the bis-tetrachloropropyl ether molecule, to which its stability under these conditions is to be attributed.

EXPERIMENTAL

Preparation of Divinyl Ether. Divinyl ether was prepared by the previously described method [8]. Bis-2-chloroethyl ether (40 g) was added slowly to a stirred mixture of 100 g of potassium hydroxide powder and 15 g of triethanolamine at 160°. The divinyl ether, amounting to 12.5 g (65%), was collected in a trap; it had b.p. 28-28.5° and $n^{20}D$ 1.3980.

The literature [8] gives b.p. 28.3-28.5° (752 mm) and $n^{20}D$ 1.3982.

Reaction of Divinyl Ether with Carbon Tetrachloride. A mixture of divinyl ether, carbon tetrachloride, and initiator was prepared in a flask fitted with thermometer, stirrer, and reflux condenser attached to spiral trap cooled to −25°. The reaction mixture was stirred and heated to a gentle boil (68-84°; 3 hours). The mixture was cooled, excess of carbon tetrachloride was distilled off, and the residue was vacuum-fractionated. Thus, from 14 g of divinyl ether, 49.0 g of carbon tetrachloride, and 0.6 g of 2,2'-azobis[2-methylpropionitrile] we obtained 56.8 g of colorless crude product, from which we isolated the following fractions:

Fraction I b.p. 53-55° (3 mm); 7.7 g
Fraction II b.p. 127-130° (3 mm); 37.5 g
Residue   8.1 g

From Fraction I we isolated a product having the following constants: b.p. 87.5° (23 mm); 93° (27.5 mm); 78.5° (14 mm); $n^{20}D$ 1.4849; d^{20}_4 1.3874; Found : MR = 46.24; Calculated MR for $C_5H_6OCl_4$ ⊢ 45.93.

Found %: C 27.10; 26.73; H 2.63; 2.77 $C_5H_6OCl_4$. Calculated %: C 26.81; H 2.70.

Found M: 209.79; 209.40 $C_5H_6OCl_4$. Calculated M: 223.93.

This compound corresponded in constants to 1,3,3,3-tetrachloropropyl vinyl ether (I). Yield 17.2%. Fraction II gave a product having the following constants: b.p. 120.0 - 120.5° (0.5 mm); 133-133.5° (3.5 mm); $n^{20}D$ 1.5133; $d^{20}D$ 1.6133; Found MR 70.41; Calculated for $C_6H_6OCl_8$ MR 70.49.

Found %: C 19.63; 19.60; H 1.50; 1.53; Cl 74.38; 74.91 $C_6H_6OCl_8$. Calculated %: C 19.07; H 1.60; Cl 75.09.

Found M: 366.27; 373.20 $C_6H_6OCl_8$. Calculated M: 377.76.

This compound was bis-1,3,3,3-tetrachloropropyl ether (II); yield 50.0%. The results of experiments typical for these conditions are given in the table.

Hydrogenation of 1,3,3,3-Tetrachloropropyl Vinyl Ether (I). Equation (c). 1,3,3,3-Tetrachloropropyl vinyl ether (3.0 g) was hydrogenated as a solution in 15 g of dioxane over an Adams platinum catalyst at room

temperature. In the course of five hours 330 ml (theoretical amount 340 ml) of hydrogen was absorbed. Fractionation gave 2.4 g of ethyl 1,3,3,3-tetrachloropropyl ether having the following constants: b. p. 85-86° (15 mm); $n^{20}D$ 1.4710; d^{20}_4 1.3480. The literature [1] gives b.p. 72.5° (8 mm); $n^{20}D$ 1.4700; d^{20}_4 1.3472.

TABLE 1

Reaction of Divinyl Ether with Carbon Tetrachloride

Experiment	Initial molar ratio of divinyl ether and CCl$_4$	Amount of initiator (% on ether)	Experimental conditions	Yield of tetrachloropropyl ether (%)	Yield of bis-tetrachloropropyl ether (%)	Yield of macromolecular residue (% on crude product)	
1	1 : 4	1,0	2 hours at 30°	—	9,3	—	With 2,2'-azobis [2-methylpropionitrile]
2	1 : 1	1,3*	3 hours at 80°	17.8	—	50.0	
3	1 : 2	2,6*	ditto	14.0	—	43.0	
4	1 : 2	2,0	3 hours at boil (80°)	2.2	26.5	44.5	
5	1 : 4	4,0	ditto	13.7	37.2	29.1	
6	1 : 8	2,0	"	13.4	36.6	13.2	
7	1 : 8	4,0	»	18.5	56.5	15.0	
8	1 : 16	4,0	»	21.0	47.4	13.5	
9	1 : 8	2,0	»	35.0	18.0	11.0	With benzoyl peroxide
10	1 : 8	4,0	»	2.2	61.2	27.0	
11	1 : 16	4,0	»	2.2	75.0	23.4	

• Saturated solution of the azo dinitrile in CCl$_4$.

Hydrolysis of 1,3,3,3-Tetrachloropropyl vinyl Ether (I). Equation (d). A mixture of 5.7 g of tetrachloropropyl vinyl ether and 25 ml of distilled water was heated under reflux for two hours at 80-82° with stirring. The lower layer was dissolved in ether and washed three times with water to free it from acetaldehyde. The ether solution was dried over sodium sulfate, and after removal of ether we obtained 1.8 g of 3,3-dichloroacrolein, b.p. 48° (40 mm) and $n^{20}D$ 1.5065. The literature [2] gives b.p. 57° (49 mm) and $n^{20}D$ 1.5050. The semicarbazone of the dichloroacrolein melted at 166.5° (from alcohol); % N : 23.27; 23.13; calculated for $C_4H_5ON_3Cl_2$ %N: 23.10.

The aqueous layer of the hydrolyzate smelled of acetaldehyde and gave a positive reaction with Schiff's reagent.

Hydrolysis of Bis-1,3,3,3-tetrachloropropyl Ether (II). a) A mixture of 1 g of bis-tetrachloropropyl ether and 20 ml of distilled water was sealed in a tube, which was heated in a boiling water bath for 12 hours with periodic shaking. When cool, the oily layer was extracted with ether, dried, and distilled. This gave 0.82 g of bis-tetrachloropropyl ether; b.p. 157° (9 m); $n^{20}D$ 1.5135; d^{20}_4 1.6052. The ether was recovered unchanged; the aqueous layer of the hydrolyzate did not give a positive reaction with Schiff's reagent.

b) A mixture of 3 g of bis-tetrachloropropyl ether and 25 ml of 2% sulfuric acid was boiled in a flask fitted with stirrer for six hours. Most of the ether (2.45 g) was recovered unchanged; b.p. 127° (0.5 mm); $n^{20}D$ 1.5135.

SUMMARY

1. The conditions for reaction between divinyl ether and carbon tetrachloride in presence of benzoyl peroxide or 2,2'-azobis [2-methylpropionitrile] were studied.

2. The conditions for the formation of 1,3,3,3-tetrachloropropyl vinyl and bis-1,3,3,3-tetrachlorovinyl ethers were found. The ethers isolated were characterized, and the structure of tetrachloropropyl vinyl ether was proved by hydrolysis and hydrogenation.

3. It was shown that bis-1,3,3,3-tetrachloropropyl ether has exceptional stability in hydrolysis reactions.

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CARBON-CHAIN POLYMERS AND COPOLYMERS

COMMUNICATION 4. SYNTHESIS AND POLYMERIZATION
OF METHYL p-VINYLBENZOATE

G. S. Kolesnikov and T. A. Soboleva

In an investigation on the preparation of alkoxystyrenes and their polymerization one of us in collaboration with Pogosian [1, 2] found that the glass-transition temperatures of p-alkoxystyrene polymers are much higher than those of p-alkylstyrene polymers. In explanation of the higher glass points of p-alkoxystyrene polymers we suggested that the cause lie in the formation of hydrogen bonds between the oxygen atom of the alkoxy group and the hydrogen atom of the aromatic nucleus.

In continuation of work on the synthesis and polymerization of styrene derivatives containing substituents in the aromatic nucleus, we undertook the synthesis of methyl p-vinylbenzoate with the object of determining the effect of the introduction of an ester grouping into the styrene molecule on the glass point of the polymer. It might be supposed that the introduction of an ester grouping into the styrene molecule would lead to rise in the glass point of the polymer, because oxygen in a carbonyl group forms a stronger hydrogen bond than the oxygen of an alkoxy group; on the other hand the ester grouping might have just the opposite effect because of the plasticizing effect peculiar to esters.

The synthesis of methyl p-vinylbenzoate was carried out in the following steps: p-dibromobenzene → p-bromo-α-methylbenzyl alcohol → p-1-hydroxyethylbenzonitrile → p-vinylbenzonitrile → methyl p-vinylbenzoate. Methyl p-vinylbenzoate was converted into a polymer by heating it in presence of 0.137 mole per cent of benzoyl peroxide for 120 hours with rise in temperature from 40° to 120°; under the same conditions in presence of 0.156 mole per cent of benzoyl peroxide we prepared a copolymer of 79.96 moles per cent of methyl methacrylate and 20.04 moles per cent of methyl p-vinylbenzoate. The polymer and copolymer were precipitated with methanol from their solutions in benzene, and their glass points (second-order transition points) and intrinsic viscosities were determined. It was found that the glass point of methyl p-vinylbenzoate polymer is 133°, and that of the copolymer with methyl methacrylate is 120°; analysis of the reprecipitated copolymer showed that it contained 16.2 moles per cent of methyl p-vinylbenzoate residues. The intrinsic viscosities were 1.15 for the methyl p-vinylbenzoate polymer and 1.12 for the copolymer (20°; solution in toluene).

Methyl p-vinylbenzoate was first prepared by Marvel and Overberger [3]; for the polymer of this compound they give a softening point of 205-212°, but do not indicate the method of determination.

Our results show that the introduction of an ester grouping into the styrene molecule results in a rise in the glass point of the polymer, which in our opinion, is a consequence of the formation of hydrogen bonds between oxygen atoms of carboxy groups and hydrogen atoms of aromatic nuclei.

EXPERIMENTAL

p-Bromo-α-methylbenzyl Alcohol. A mixture of 27 g of magnesium, a crystal of iodine, and 100 ml of a solution of 236 g of p-dibromobenzene in 700 ml of dry ether was prepared in a flask fitted with stirrer, reflux condenser, and dropping funnel. The mixture was heated until reaction set in, and the rest of the solution was then added gradually. The mixture was boiled until all of the magnesium had dissolved, and

it was then stirred and cooled with ice while a cooled solution of 45 g of acetaldehyde in 200 ml of dry ether was added gradually. The mixture was set aside overnight without cooling, and it was then decomposed with 3-5% acetic acid solution. After suitable treatment of the ethereal solution, vacuum distillation gave 98 g (50%) of p-bromo-α-methylbenzyl alcohol, b.p. 130-140° (12 mm).

p-1-Hydroxyethylbenzonitrile. A mixture of 60 g of p-bromo-α-methylbenzyl alcohol, 25 g of cuprous cyanide, 55 ml of pyridine, 1 g of hydroquinone, 2 drops of p-tolunitrile, and two crystals of copper sulfate was refluxed for 15 hours in a bath of Wood's metal at 190-210°. The hot mixture was poured into a mixture of 150 ml of aqueous ammonia and 150 ml of water, 150 ml of benzene was added, and the whole was shaken vigorously. The mixture was cooled to room temperature, and 150 ml of ether was added. Without first separating the layers the mixture was filtered; the organic layer was then separated and washed several times with dilute aqueous ammonia, then with 6 N HCl, then with water, and finally with saturated sodium chloride solution. The solution was dried with sodium sulfate, and ether and benzene were distilled off. Vacuum distillation gave 25 g (55.6%) of p-1-hydroxyethylbenzonitrile, b.p. 136-141° (5mm).

p-Vinylbenzonitrile. A mixture of 8.5 g of powdered fused potassium hydrogen sulfate and 2.5 g of hydroquinone was prepared in a Claisen flask. Air was displaced with oxygen-free nitrogen, the contents of the flask were heated in a bath of Wood's metal to 220-230°, the pressure was reduced to 40-45 mm, and 16 g of p-1--hydroxyethylbenzonitrile was added dropwise with continued passage of nitrogen; at the end of the reaction the temperature had risen to 240-250°. The reaction products that had distilled over were dissolved in ether,and the solution was washed with 5% potassium hydroxide solution and saturated calcium chloride solution; it was dried with calcium chloride, and ether was distilled off. Vacuum distillation of the residue gave 13.4 g (46%) of p-vinylbenzonitrile, b.p. 88-91° (3 mm). For p-vinylbenzonitrile the literature [3] gives b.p. 102-104° (9 mm).

p-Vinylbenzoic Acid. A solution of 5 g of p-vinylbenzonitrile, 8.1 g of potassium hydroxide, and 0.2 g of hydroquinone in 50 ml of alcohol was refluxed for 12 hours. The precipitated potassium p-vinylbenzoate was filtered off and dissolved in water; the solution was acidified with hydrochloric acid, and the p-vinylbenzoic acid liberated was filtered off. Recrystallization of the product from 20% alcohol in presence of a little hydroquinone gave 4 g (6 7%) of p-vinylbenzoic acid, m.p. 142-144°.The literature [3] gives m.p. 143-144°.

Methyl p-Vinylbenzoate. A solution of 6 g of p-vinylbenzoic acid in 200 ml of methanol was saturated with hydrogen chloride in the cold, and the solution was set aside at 0° for 24 hours. Methanol was allowed to evaporate, and the methyl p-vinylbenzoate that remained was crystallized from aqueous alcohol in presence of hydroquinone. The yield of methyl p-vinylbenzoate, m.p. 31-33°, was 6 g (85%). Before being polymerized, methyl p-vinylbenzoate was dissolved in benzene, the solution was filtered and washed, first 2-3 times with 5% caustic alkali solution and then 3-4 times with water, benzene was removed under vacuum (without heating the solution), and the residue was vacuum-dried at room temperature. The methyl p-vinylbenzoate purified in this way melted at 34.5-35.5°. For methyl p-vinylbenzoate the literature [3] gives m.p. 35-36°.

The glass points of the polymer and copolymer of methyl p-vinylbenzoate were determined by B. L. Tsetlin, to whom we express our thanks.

SUMMARY

Methyl p-vinylbenzoate was synthesized; its polymer and its copolymer with methyl methacrylate were prepared, and their glass points (second-order transition points) were determined.

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*Original Russian pagination. See C.B. translation.

SYNTHESIS OF POLYALKYLENEARYLS

COMMUNICATION 7. COPOLYCONDENSATION IN THE SYSTEMS 1,2-DICHLOROETHANE-BENZENE-FLUOROBENZENE AND 1,2-DICHLOROETHANE-CHLOROBENZENE-FLUOROBENZENE

We have previously reported the results of a study of the copolycondensation of 1,2-dichloroethane with benzene and chlorobenzene [1-3]. In order to find out how other halobenzenes behave in copolycondensations with dichloroethane and benzene in presence of aluminum chloride, we investigated the systems dichloroethane-benzene-fluorobenzene and dichloroethane-chlorobenzene-fluorobenzene. For comparison purposes, we carried out the polycondensation of dichloroethane with fluorobenzene under the same conditions; the polycondensation of dichloroethane with fluorobenzene was first studied by two of us in collaboration with Fedorova [4].

EXPERIMENTAL

The polycondensation conditions used in the present investigation were as follows: the ratio of total aromatics to dichloroethane was 1.5 : 1, the catalyst concentration was 3 moles per cent on the total aromatic compounds, the reaction temperature was 65°.
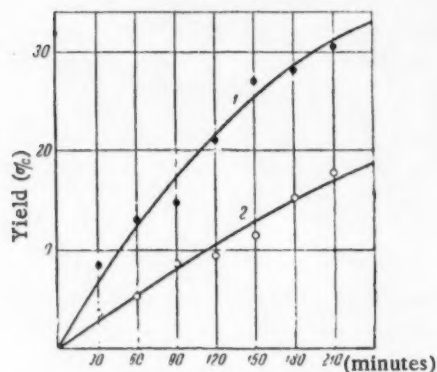

Fig. 1. Relation of yield of copolymer to duration of reaction in the systems: 1) benzene-chlorobenzene-dichloroethane; 2) benzene-fluorobenzene-dichloroethane.
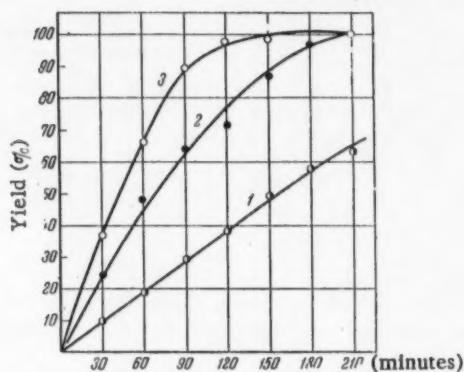
Fig. 2. Relation of yield of polymer to duration of reaction in the systems: 1) benzene-dichloroethane; 2) fluorobenzene-dichloroethane; 3) chlorobenzene-dichloroethane.

Dichloroethane-Benzene-Fluorobenzene. With a benzene : fluorobenzene ratio of 1 : 1 the polycondensation product was found to contain only traces of fluorine; this indicates the low relative activity of fluorobenzene, its activity being lower than that of chlorobenzene, which under these conditions participates in the building up of the copolymer molecule [3]. When the concentration of fluorobenzene in the original mixture is increased, it begins to take part in the copolycondensation reaction. Table 1 and Fig. 1 give the results of the

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copolycondensation of dichloroethane with benzene and fluorobenzene for a benzene : fluorobenzene ratio of 1 : 10. The ratio $\underline{n}/\underline{m}$ of the fragments $-C_6H_4CH_2CH_2-$ and $-C_6H_3FCH_2CH_2-$ in the copolymer is given by the formula

$$n/m = \frac{18,27}{F,\%} - 1.173,$$

in which F is the fluorine content (%) of the copolymer.

It will be seen from Table 1 and Fig. 1 that with increase in the duration of reaction, the yield of copolymer increases, the content of fluorine-containing fragments increases, and the degree of polymerization of the copolymer increases. However, when we compare this with polycondensation in the system benzene-chlorobenzene-dichloroethane under the same conditions [3] it is notable that the yields of copolymer in the system benzene-fluorobenzene-dichloroethane are, for a given duration of reaction, only about one-half of those in the chlorobenzene system, though the degree of polymerization of the copolymer is somewhat higher. The ratio $(C_6H_4CH_2CH_2)$: $(C_6H_3XCH_2CH_2)$ in the copolymer obtained in the copolycondensation of dichloroethane with benzene and fluorobenzene is higher than the same ratio for the copolymer from dichloroethane, benzene, and chlorobenzene. This indicates that fluorobenzene has a lower relative activity than chlorobenzene.

It was found also that the polycondensation of fluorobenzene with dichloroethane is very rapid and is intermediate in this respect between the polycondensation of dichloroethane with benzene and that of dichloroethane with chlorobenzene, as will be seen by a comparison between the data in Table 2 and previously published results [3] obtained under the same conditions. The intermediate position of fluorobenzene between benzene and chlorobenzene in their polycondensations with dichloroethane was first pointed out by two of us and Fedorova [4].

TABLE 1

Copolycondensation of Dichloroethane with Benzene and Fluorobenzene

Duration of reaction (minutes)	Yield of copolymer (%)	Fluorine content of copolymer (%) (mean)	n/m	Basal molar weight of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	3.5	6.96	1.45	111.3	—	—
60	5.3	7.04	1.42	111.4	—	—
90	8.5	8.69	0.93	113.3	—	—
120	9.4	8.85	0.89	113 4	2310	20.4
150	11.4	8.95	0.87	113.6	2320	20.4
180	15.2	9.02	0.85	113.7	2410	21.1
210	17.6	10.37	0.61	115.2	2610	22.6

For comparison purposes, in Fig. 2 we give results on polycondensation in the systems benzene-dichloroethane, fluorobenzene-dichloroethane, and chlorobenzene-dichloroethane.

Dichloroethane-Chlorobenzene-Fluorobenzene. As the relative activity of fluorobenzene was found to be considerably lower than that of benzene (for polycondensation with dichloroethane) it was of interest to study polycondensation in the system dichloroethane-chlorobenzene-fluorobenzene, for in this case the relative activities of the aromatic components differ to a smaller extent than in systems containing benzene and one of these halobenzenes. We carried out the copolycondensation of dichloroethane with chlorobenzene and fluorobenzene under the conditions indicated above; the chlorobenzene : fluorobenzene ratio was 1:1; the ratio n/m of the fragments $-C_6H_3ClCH_2CH_2-$ and $C_6H_3FCH_2CH_2-$ was determined from the formula

$$n/m = \frac{13,71}{F,\%} - 0.8809,$$

The results are given in Table 3 and Fig. 3.

TABLE 2

Polycondensation of Dichloroethane with Fluorobenzene (fluorobenzene :
: dichloroethane = 1.5 : 1; 3 moles % of $AlCl_3$ on fluorobenzene; 65°)

Duration of reaction (minutes)	Yield of polymer (%)	Molecular weight of polymer	Degree of polymerization
30	24.3	1560	12.8
60	48.3	1960	16.1
90	63.7	1960	16.1
120	71.4	2000	16.4
150	87.1	2120	17.4
180	97.2	2200	18.0

TABLE 3

Copolycondensation of Dichloroethane with Chlorobenzene and Fluorobenzene

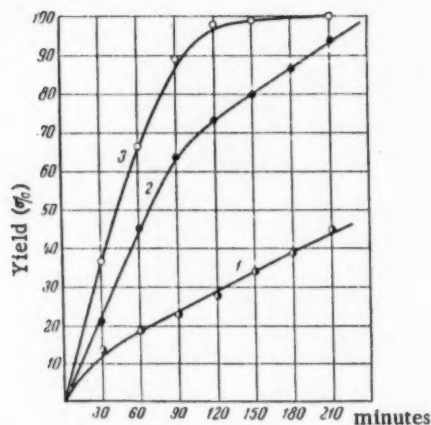| Duration of reaction (minutes)	Yield of copolymer (%)	Fluorine content of copolymer (%) (mean)	n/m	Basal molar weight of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	20.2	5.08	1.8	132.6	1530	11.5
90	63.3	4.18	2.4	133.6	1690	12.6
120	72.8	4.43	2.2	133.4	1760	13.2
150	79.4	5.26	1.7	132.5	1890	14.2
180	86.5	4.77	2.0	133.0	2120	16.0
210	93.3	4.83	2.0	132.9	2120	16.0

Fig. 3. Relation of yield of polymer to duration in the systems: 1) benzene-
-chlorobenzene-dichloroethane; 2) fluorobenzene-chlorobenzene-dichloro-
ethane.

It will be seen from Table 3 and Fig. 3 that as the duration of reaction is increased, the yield and degree of polymerization of the copolymer increase. The rate of polycondensation in the system dichloroethane-fluoro-benzene-chlorobenzene is considerably greater than in the system dichloroethane-benzene-chlorobenzene and approximates to the rates in the separate polycondensations of dichloroethane with chlorobenzene and with flurobenzene. This is probably to be explained by the fact that there is not such a great difference between the relative activities of fluorobenzene and chlorobenzene in this system as there is between benzene and fluorobenzene or benzene and chlorobenzene, and the polycondensation process is not retarded by any component of the reaction system. The value of n/m indicates that the relative activity of chlorobenzene in its reaction with dichloroethane is about twice that of fluorobenzene.

SUMMARY

1. A study was made of copolycondensation in the systems 1,2-dichloroethane-benzene-flurobenzene and 1,2-dichloroethane-chlorobenzene-fluorobenzene.

2. The relative activity of fluorobenzene is only about one-half of that of chlorobenzene.

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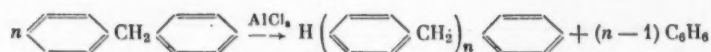
SYNTHESIS OF POLYALKYLENEARYLS

COMMUNICATION 8. TRANSARYLATION OF DIPHENYLMETHANE

### G. S. Kolesnikov, V. V. Korshak, and T. V. Smirnova

Two of us [1, 2] have previously studied the transarylation of bibenzyl in presence of aluminum chloride and have determined the effect of reaction temperature and catalyst concentration on the course of the process. In continuation of investigations in this direction we undertook the study of the transarylation of diphenylmethane, as being the simplest diarylalkane. The experimental procedure was the same as in the transarylation of bibenzyl [1].

We found that diphenylmethane undergoes transarylation in presence of aluminum chloride, the rate of reaction being appreciable at 80° and above; at lower temperatures transarylation is very slow. Diphenylmethane was found to be less reactive than bibenzyl, the transarylation of which proceeds at an appreciable rate already at 60°. In order to determine the effect of temperature on the couse of the transarylation of diphenylmethane in presence of aluminum chloride, we carried out four series of experiments in which the aluminum chloride concentration was kept constant at 5.1 moles per cent on the diphenylmethane and the temperature was 80°, 90°, 100°, and 105°, respectively. The results are presented in Tables 1-4.

It will be seen from Tables 1-4 that the yield of polymethylenephenyl, the macromolecular transarylation product from diphenylmethane, increases with increase in the duration of reaction; at the same time the amount of unchanged diphenylmethane diminishes. A low-molecular-weight product of the transarylation of diphenylmethane was benzene, which was identified both by its physical properties and by its conversion through nitrobenzene and aniline into acetanilide.

$$n \left\langle \underset{}{\bigcirc} \right\rangle CH_2 \left\langle \underset{}{\bigcirc} \right\rangle \xrightarrow{AlCl_3} H \left(\left\langle \underset{}{\bigcirc} \right\rangle CH_2 \right)_n \left\langle \underset{}{\bigcirc} \right\rangle + (n-1) C_6H_6$$

Tables 1-4 show also that the increase in the yield of polymethylenephenyl with prolongation of the reaction and rise in the temperature is not accompanied by increase in the molecular weight of the polymethylenephenyl, particularly at the later stages of the process. The molecular weight of the polymethylenephenyl formed is low and is almost constant in all the experiments carried out. The formation of a polymethylenephenyl of low molecular weight in the transarylation of diphenylmethane is reminiscent of the polycondensation of methylene chloride with benzene in presence of aluminum chloride, which also gave a polymethylenephenyl of low molecular weight [3]. As in the case of the polycondensation of methylene chloride with benzene, the low molecular weight of the polymethylenephenyl can, in our opinion, be explained by the formation of dihydroanthracene ring systems at the ends of the growing chain with resulting cessation of chain growth. It is known that anthracene is formed when diphenylmethane is heated with aluminum chloride [4]; this reaction proceeds under more severe conditions than the transarylation reaction, but the formation of 9,10-dihydroanthracene as an intermediate product under the conditions of the transarylation reaction seems to us to be extremely probable:
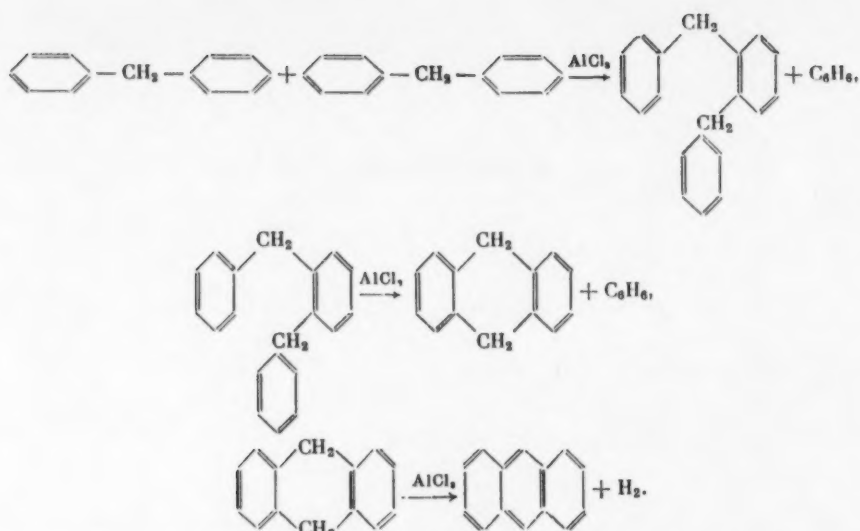
Such a scheme for the formation of dihydroanthracene was proposed earlier by two of us [5].

TABLE 1

Transarylation of Diphenylmethane at 80°

Duration of reaction (minutes)	Yield of		Molecular weight of polymethylenephenyl (%)
	diphenylmethane (% of amount taken)	polymethylenephenyl (%)	
10	69.6	25.3	1590
20	48.8	44.4	1190
35	52.4	47.8	1420
50	32.7	74.4	1210
60	25.0	82.4	1380

TABLE 2

Transarylation of Diphenylmethane at 90°

Duration of reaction (minutes)	Yield of		Molecular weight of polymethylenephenyl (%)
	diphenylmethane (% of amount taken)	polymethylenephenyl (%)	
10	58.3	38.9	670
20	58.3	41.1	1220
30	51.8	55.5	900
35	24.4	83.3	1220
40	34.6	75.5	1070
60	27.9	84.4	1350

TABLE 3

Transarylation of Diphenylmethane at 100°

Duration of reaction (minutes)	Yield of		Molecular weight of polymethylenephenyl (%)
	diphenylmethane (% of amount taken)	polymethylenephenyl (%)	
10	17.8	82.2	990
20	24.4	88.9	1220
30	19.0	90.0	1180
40	15.5	91.1	1640
60	13.7	94.0	1440

TABLE 4

Transarylation of Diphenylmethane at 105°

Duration of reaction (minutes)	Yield of		Molecular weight of polymethylenephenyl (%)
	diphenylmethane (% of amount taken)	polymethylenephenyl (%)	
10	26.8	82.2	580
20	26.8	86.6	550
30	17.8	88.9	1200
40	14.0	87.8	1140
60	12.8	88.9	1670

The polymethylenephenyl obtained in all the above-described experiments was soluble in benzene, dichloroethane, carbon tetrachloride, and other aromatic and chlorinated solvents. The formation of a cross-linked polymer was not observed.

In order to determine the effect of temperature on the course of the transarylation of diphenylmethane, we

carried out a series of experiments in which the catalyst concentration was kept constant at 5.1 moles per cent on the diphenylmethane, the duration of reaction was constant at 60 minutes but the reaction temperature was varied from 80° to 200°. The results are given in Table 5.

TABLE 5

Transarylation of Diphenylmethane at Various Temperatures

Reaction temperature (°C)	diphenyl-methane (% of amount taken)	Yield of polymethylenephenyl (%)		Molecular weight of polymethylenephenyl (%)
		total	cross-linked component	
80	25.0	82.4	—	1380
90	27.9	84.4	—	1350
100	13.7	94.4	—	1440
105	12.8	88.9	—	1670
110	10.1	91.2	—	1710
120	8.9	88.2	—	1850
130	7.1	100.0	—	1470
140	5.4	82.2	—	1890
150	Traces	100.0	—	1500
160	"	77.7	—	2010
170	—	84.4	13.3	1790
180	—	95.5	20.0	1670
190	—	88.8	31.1	2140
200	—	81.1	27.1	2350

It will be seen from Table 5 that rise in reaction temperature from 80° to 160° leads to increase in the yield of polymethylenephenyl. From 170° upward, the yield of soluble polymethylenephenyl begins to fall, and some cross-linked polymer, insoluble in benzene and other organic solvents, begins to form in amounts increasing as the temperature rises. The formation of cross-linked reaction products only at high temperatures gives us reason to suppose that in the transarylation of diphenylmethane the formation of dihydroanthracene ring systems proceeds more readily than the formation of branched and cross-linked polymer molecules, such as occurs in the polycondensation of methylene chloride with benzene in presence of aluminum chloride [3]. Rise in the temperature of the transarylation of diphenylmethane is accompanied by rise in the molecular weight of the polymethylenephenyl; this can probably be attributed to increase in the reactivity of the end groups of poly-methylenephenyl as the temperature rises.

As the transarylation of diphenylmethane is a catalytic process, some work was carried out on the effect of catalyst concentration, the reaction temperature being kept constant at 90° and the catalyst concentration varied. The results of these experiments are given in Tables 2, 6, and 7.

TABLE 6

Transarylation of Diphenylmethane in Presence of 7.4 moles per cent of Aluminum Chloride

Duration of reaction (minutes)	Yield of		Molecular weight of polymeth-ylenephenyl (%)
	diphenyl-methane (% of amount taken)	polymethylene phenyl (%)	
10	57.1	42.2	1430
20	35.7	73.3	1180
30	19.6	83.3	1680
40	26.8	80.0	1620
60	20.8	97.7	1360

TABLE 7

Transarylation of Diphenylmethane in Presence of 8.9 moles per cent of Aluminum Chloride

Duration of reaction (minutes)	Yield of		Molecular weight of polymeth-ylenephenyl (%)
	diphenyl-methane (% of amount taken)	polymethylene phenyl (%)	
10	30.4	76.6	1270
20	24.4	81.1	1200
30	25.6	85.5	1070
40	16.1	93.3	1730
60	14.9	93.3	1580

It will be seen from Tables 2, 6, and 7 that the catalyst concentration has a substantial effect on the rate of the transarylation of diphenylmethane, the behavior being similar to that observed by two of us in the transarylation of bibenzyl [2]: with increase in the aluminum chloride concentration, the rate of transarylation increases. It should be noted that increase in catalyst concentration has no effect on its molecular weight. In spite of the increase in the concentration of catalyst, the formation of cross-linked products was not observed.

We consider that the mechanism of the transarylation of diphenylmethane is analogous to that suggested previously by two of us for the transarylation of bibenzyl [6]; the difference consists in the possibility of the formation of dihydroanthracene ring systems in the transarylation of diphenylmethane, both at the ends of a growing chain and within the chain.

The transarylation of diphenylmethane in presence of aluminum chloride was studied at various temperatures and catalyst concentrations.

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Institute of Heteroorganic Compounds of the
Academy of Sciences of the USSR   Received November 20, 1956

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VALENCE-VIBRATION FREQUENCIES AND ELECTRONIC BOND
CHARGES FOR C — H BONDS IN HYDROCARBONS

G. V. Bykov

In the graph (see Figure) we have plotted points having as abscissae the values calculated previously [1, 2] of total (σ - + π -) electronic charges of C — H bonds in allene, ethylene, benzene, and acetylene and of σ -electronic charges in ethane and methane and having as ordinates the corresponding frequencies of symmetrical valence vibrations of these bonds (see table). As will be seen from the figure, these points (o) fit well to the straight line 1. The electronic charge in methane does not require calculation; the charge of the C — H bond in ethane was calculated by the formula proposed by the author

$$A_{CH} = 1 + \frac{4}{\Sigma E,}$$

in which ΣE is the sum of the electronegativities of the atoms attached to the given carbon atom. The charges of bonds in the other hydrocarbons were found by a more complicated method by the use of a formula expressing the logarithmic relationship between electronic charges and frequencies and deduced on the basis of the already calculated value of the charge of the C — H bond in ethane.

TABLE

Compound	$A_{CH}^{\sigma\pi}$ (electrons)	ν_{CH} (cm^{-1}) [3]
Methane	2.000	2914*, 3020
Ethane	1.955	2880*, 2925, 2940, 2980
Ethylene	2.095	2989, 3019*, 3070, 3105
Allene	2.069	2992*, 3062
Benzene	2.138	3045, 3064*, 3095
Acetylene	2.445	3285, 3372*

• The asterisks indicate frequences of symmetrical vibrations.

The electronic charges of bonds in acetylene can be determined also in another way, i.e. from thermochemical data only. This method, which we cannot discuss further here owing to lack of space (see following communication), gives the following values of electronic charges of C — H bonds in acetylene: A_{CH}^{σ} =1.720 (1.723), A_{CH}^{π} = 0.720 (0.723), $A_{CH}^{\sigma\pi}$ = 2.440 (2.445), which are very close to the results obtained previously [1] (given in parentheses for comparison purposes).

By the method given in [2], on the basis of the value of the π -electronic charge of the C —C bond in ethylene A_{CC}^{π} 1.333(Scherr [4]), we find that in this hydrocarbon $A_{CH}^{\sigma\pi}$ =2.105. The corresponding point (□) also lies close to the straight line 1.

In the graph we have plotted the remaining points for the valence vibrations of C — H bonds against the previously calculated values of A_{CH}^{π} [1,2] for the various compounds (denoted by △). It was found that it was

possible to draw a straight line 2 on which or near to which (ethane) there lies one point for each compound. Hence, two horizontals corresponding to vibrations of C − H bonds in a given hydrocarbon intersect the straight lines 1 and 2 at points that lie one above the other. However, if symmetrical vibrations are impossible, there will probably be a point on the straight line 2 corresponding to one of the frequencies of the C − H bond and its total electronic charge.

Two Examples. Propyne has three frequencies: 2928, 2975, and 3300 cm^{-1} [3]. The last of these is clearly to be attributed to the vibrations of the $C^{2\pi}$ − H bond. It is not very probable that there can be a point on the straight line 2 corresponding to a vibration frequency of the C−H bond in the methyl group of 2975 cm^{-1}, because this is extremely close to the maximum frequency of the C−H bond in ethane, whereas the difference in the charges and therefore in the frequencies of these bonds in the two compounds must be relatively great because of the difference in the electronegativities of the carbon atoms in ethane and acetylene. There remains the frequency 2928 cm^{-1}. From similar considerations we conclude that of the three frequencies in 2-butyne 2918, 2960, and 2976 cm^{-1} the frequency sought will be 2918 cm^{-1}. In further calculations we shall assume the mean value of 2923 ± 5 cm^{-1}. On the basis of the known data concerning charges, with the aid of which the straight line 2 was constructed, we shall consider simply that a certain straight line exists which on the charge-frequency diagram passes through the point
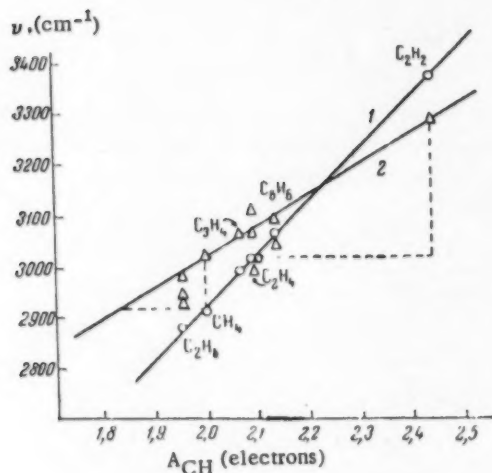
$$\left(1 + \frac{4}{3 + E_C{}^{2\pi}}, 2923 \pm 5\right)$$

(the methyl group in propyne and 2-butyne), the point (2,3020) (methane), and the point

$$\left(1 + \frac{4}{1 + E_C{}^{2\pi}}, 3285\right)$$

(acetylene). From the similarity of the triangles indicated by broken lines in the diagram it follows that

$$\frac{3020 - 2923 \pm 5}{2 - \left(1 + \dfrac{4}{3 + E_{C^{2\pi}}}\right)} =$$

$$= \frac{3285 - 3020}{1 + \dfrac{4}{1 + E_{C^{2\pi}}} - 2}$$

From which we find that $E_{C^{2\pi}} = 1.77 \pm 0.02$ and that the bond charges in acetylene are $A_{CH}^{\pi} = 0.722 \pm 0.005$ electron and $A_{CH}^{\sigma\pi} = 2.44 \pm 0.01$ electron, in excellent agreement with the results obtained by two other schemes of calculation.

The spectrum of cyclopropane contains the frequencies 3010, 3020, 3028 and 3080 cm^{-1}, one of which must belong to the symmetrical valence vibration of the C − H bonds. From the graph it can be shown that the horizontals corresponding to the last two frequencies intersect the straight lines 1 and 2 at points lying almost one above the other at $A_{CH}^{\sigma} \approx$ about 2.1 electrons. Hence, in cyclopropane, as in benzene [2], because

of the mutual repulsion of the bonds and electron shells of carbon atoms, there is a displacement of σ-electronic charges from C − C bonds to C − H bonds, a phenomenon that is probably characteristic in various degrees for other flat rings. The electronic charges of C − C bonds in cyclopropane, $A_{CC}^{\sigma} \approx$ about 1.8 electrons, are considerably less than the charges of C − C bonds in paraffins, which is in good accord with the tendency of cyclopropane to undergo cleavage at a C − C bond.

, There is reason to suppose, therefore, that electronic-charge—frequency diagrams can be of great value in the analysis of molecular spectra.

SUMMARY

1. It was shown that a linear relationship exists between the frequencies of valence vibrations and electronic charges of C — H bonds in si mple hydrocarbons of various classes.

2. Three different methods of calculating the electronic charges of bonds in acetylene give very similar results.

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ELECTRONIC BOND CHARGES IN ACETYLENE

G. V. Bykov

According to the theory of electronic bond charges, the total σ- and π-electronic shell of a molecule can be represented as the sum of charges localized in bonds. This theory, in the form in which it has been developed by the author, predicts the existence of π-electronic charges of $C-H$ and similar bonds formed by only a single atom-donor of π-electrons (when necessary, we indicate such atoms by a superscript such as π or 2π, depending on the number of π-electrons contributed by the atom to the π-electron shell of the molecule). As there are, as yet, no experimental methods which could give direct confirmation of the existence of such charges, not to speak of their actual values, theoretical calculations of these charges based on various data acquire great importance, since they provide material for a comparative treatment.

The calculation of the electronic charges in acetylene from thermochemical data, given below, gives results which can be compared with those of calculations from frequencies and interatomic distances. For this purpose acetylene has an advantage over other hydrocarbons in that its $C-H$ bonds have relatively high π-electronic charges, so that the relative error in the calculations will be comparatively low. Moreover, for the calculation of π-electronic charges of $C-H$ bonds in acetylene the following formula [1] is applicable:

$$A^{\pi}_{CH} = \frac{2}{1 + E_{C^{2\pi}}}, \tag{1}$$

in which A^{π}_{CH} is the π-electronic charge of the $C-H$ bond and $E_{C^{2\pi}}$ is the electronegativity of acetylenic carbon; on the other hand in the case of other hydrocarbons it is probably necessary to take account also of the angle formed by the C^{π} atom with the other atom-donor of π-electrons.

The calculation of σ-electronic charges of $C-H$ bonds is carried out by the formula [1]:

$$A^{\sigma}_{CH} = 1 + \frac{n_C}{\Sigma E}, \tag{2}$$

in which n_C is the number of σ-electrons contributed to the system by the given carbon atom and ΣE is the sum of the electronegativities of atoms attached to the C atom taking part in the $C-H$ bond.

The author [2] suggested the following semiempirical equation, which involves the summated electronic charges of the bonds ΣA and the heat of "elementization" $H^{el}_{C_nH_m}$ (equal in absolute magnitude, but opposite in sign, to the heat of formation from the elements) of the hydrocarbon C_nH_m :

$$8,054 \, \Sigma A^{\sigma}_{CC} + 32,308 \, \Sigma A^{\sigma}_{CH} + \Delta^{h\pi}_{CC} \Sigma A^{\pi}_{CC} + \Delta^{h\pi}_{CH} \Sigma A^{\pi}_{CH} = \tag{3}$$
$$= H^{el}_{C_nH_m} + 32.216 \, n + 52.089 \, m.$$

The coefficients $\Delta^{h\pi}_{CC}$ and $\Delta^{h\pi}_{CH}$ of the summated π-electronic charges of $C-C$ and $C-H$ bonds have already been calculated [2], account being taken of the electronic charges in acetylene, as determined from spectroscopic data. However, $\Delta^{h\pi}_{CC}$ can be found in the course of our calculation without recourse to these data, and the value of $\Delta^{h\pi}_{CH}$ is not required.

, As $\Sigma A^\sigma_{CC} = N^\sigma_{C_n H_m} - \Sigma A^\sigma_{CH}$, a $\Sigma A^\pi_{CC} = N_{C_n H_m} - \Sigma A^\pi_{CH}$, in which $N^\sigma_{C_n H_m}$ and $N^\pi_{C_n H_m}$ are respectively the number of σ- and π-electrons in the molecule, we may transform Equation (3) as follows:

$$24{,}254\,\Sigma A^\sigma_{CH} + \Delta^{h\pi}_{CC} N^\pi_{C_n H_m} + (\Delta^{h\pi}_{CH} - \Delta^{h\pi}_{CC})\,\Sigma A^\pi_{CH} = \tag{4}$$
$$= H^{el}_{C_n H_m} + 32{,}216\,n + 52{,}089\,m - 8{,}054\,N^\sigma_{C_n H_m}.$$

In this equation we shall substitute the respective values from Table 1 for ethylene $C^\pi H_2 = C^\pi H_2$, 2,3-dimethyl--2-butene $C^\pi(C\,H_3)_2 = C^\pi(C'\,H_3)_2$, and 1,4-pentadiene $C^\pi H_2 = C^\pi H - C^*H_2 - C^\pi H = C^\pi H_2$

$$24{,}254\cdot 4\,A^\sigma_{C^\pi H} + 2\Delta^{h\pi}_{CC} + (\Delta^{h\pi}_{CH} - \Delta^{h\pi}_{CC})\cdot 4 A^\pi_{C^\pi H} = 179{,}752; \tag{5}$$

$$24{,}254\cdot 12\,A^\sigma_{C'H} + 2\Delta^{h\pi}_{CC} = 560{,}438; \tag{6}$$

$$24{,}254\cdot(6\,A^\sigma_{C^\pi H} + 2A^\sigma_{C'H}) + 4\Delta^{h\pi}_{CC} + (\Delta^{h\pi}_{CH} - \Delta^{h\pi}_{CC})\cdot 6 A^\pi_{C^\pi H} = 359{,}296. \tag{7}$$

Let us subtract (7) from the sum of (5) and (6), after first multiplying (5) by 1.5 and (6) by 0.5. In the subtraction we make an assumption that is typical for thermochemical calculations by an additive scheme, namely that all the C^π–H bonds in ethylene and 1,4-pentadiene are identical with respect to the values of their electronic charges; we then have:

$$24{,}254\cdot(6A^\sigma_{C'H} - 2A^\sigma_{C^\pi H}) = 190{,}551. \tag{8}$$

Since $E_H = 1$ and consequently, in accordance with Equation (2), $A^\sigma_{C'H'} = 1 + \dfrac{4}{3 + E_{C^\pi}}$,

and $A^\sigma_{C^*H} = 1 + \dfrac{4}{2 + 2E_{C\pi}}$, from (8) we may find the electronegativity of ethylene carbon (in the direction away from the bond with the other C^π atom): $E_{C\pi} = 1.2746$; and so also the charge: $A^\sigma_{C'H} = 1.9358$ electrons. Substituting this value in (6) we obtain $\Delta^{h\pi}_{CC} = -1.486\,(-1.54)$. In parentheses, here and later, we give figures obtained previously by another method of calculation [2]. Applying Equation (4) to 2-butyne, in which $\Sigma A^\pi_{CH} = 0$, we find that here $A^\sigma_{CH} = 1.8375$ electrons. From Equation (2) we can calculate the electronegativity of the acetylene carbon $E_{C2\pi} = 1.776\,(1.768)$; and using this and Equations (1) and (2) we can find the electronic charges of $C^{2\pi}$–H bonds in acetylene and, taking account of the fact that $N^\sigma_{C_2H_2} = 6$, and $N^\pi_{C_2H_2} = 4$, we may calculate the electronic charges of the C–C bond. The results are given in Column 1 of Table 2. We confine ourselves here to π-electronic charges, because in acetylene $A^\sigma_{CH} = A^\pi_{CH} + 1$, and $A^\sigma_{CC} = A^\pi_{CC}$.

The values in Column 2 were obtained from spectroscopic data [2], and those in Column 3 were calculated from interatomic distances [4] by a semiempirical equation, the coefficients of which clearly require some correction.

TABLE 1

Compound	$N^\sigma_{C_n H_m}$	$N^\pi_{C_n H_m}$	$H^{el}_{C_n H_m}$ (kcal/mole) [3]
Ethylene	10	2	−12.496
2,3-Dimethyl-2-butene	34	2	15.910
1,4-Pentadiene	24	4	−25.20
2-Butyne	18	4	−34.97

TABLE 2

π-Electronic Charges of Bonds in Acetylene

Bond	1	2	3
C – H	0.720	0.723	0.86
C – C	2.560	2.554	2.27

The results of the calculations, as presented in Table 2, are such that they must be regarded as a confident theoretical prediction not only of the existence of a π-electron cloud on the $C^{2\pi}-$ bond in acetylene, but also of its value of 0.7-0.8 electron. The last word lies with experiment.

SUMMARY

The electronic charges of bonds in acetylene were calculated from thermochemical data with results that are in satisfactory agreement with the results of two other calculations. A new proof was found of the localization of a π-electronic cloud amounting to 0.7-0.8 electron on the C–H bond in acetylene.

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•Original Russian pagination. See C.B. translation.

PECULIAR FEATURES OF THE OXIDATION OF CELLULOSE WITH
SODIUM PERIODATE AND WITH SODIUM CHLORITE

V. I. Ivanov, N. Ia. Lenshina, and V. S. Ivanova

In 1937-38 Jackson and Hudson applied the well-known Malaprade reaction [1] (oxidation of α-glycol groups with periodic acid) to cellulose [2]. This reaction was later studied by various authors [3-9]. It was shown that the action of periodic acid on polysaccharides, cellulose in particular results in opening of the pyran ring with formation of "dialdehydocellulose" (I). Further oxidation of preparations of (I) with sodium chlorite results in the formation of "dicarboxycellulose" with carboxy groups in the 2- and 3-positions. We studied the properties of (I) and (II) and found that, like uronic acids [10], they yield CO_2 under the conditions of Tollens decarboxylation. On the basis of our early results and spectroscopic data [11] we suggested that partial oxidation occurs at the 6-carbon atom [12].

EXPERIMENTAL

The materials taken for investigation consisted of cotton cellulose and various dialdehydo- and dicarboxy-celluloses having CHO and COOH contents, respectively, of 4.5-10%. The preparations of (I) and (II) were subjected to aqueous hydrolysis at 98° for three hours. The determination of CO_2 in the oxidized products, their hydrolyzates, and the undissolved residues was carried out under Tollens decarboxylation conditions [13]. The data on the relation between the rate of decarboxylation and the degree of oxidation are presented in Figures 1 and 2, from which it will be seen that with increase in the degree of oxidation the amount of CO_2 liberated increases. In character the curves for the rate of decarboxylation of the oxidized preparations are similar to the curves for the rate of decarboxylation of uronic acids [10], i.e. the bulk of the CO_2 is liberated in the period of decarboxylation usually used in this method. The analysis of the products of aqueous hydrolysis are given in the Table and in Figures 3 and 4. It will be seen from the table that the greater part of the decarboxylated products pass into the hydrolyzate and the sum of the amounts of CO_2 liberated from the hydrolyzate and the undissolved residue is equal to the total amount of CO_2 in the original material.
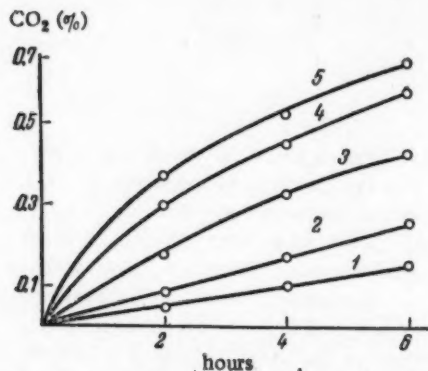

Fig. 1. Decarboxylation of dialdehydocellu-
loses: 1) unoxidized cellulose; 2) 4.5% CHO;
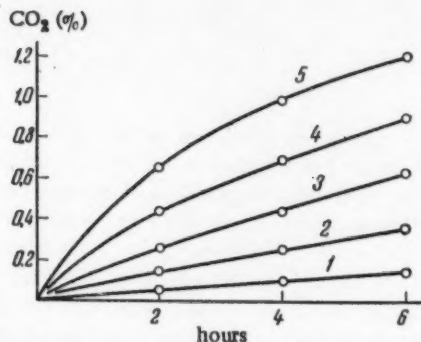3) 5.3% CHO; 4) 7.8% CHO; 5) 10% CHO.

Fig. 2. Decarboxylation of dicarboxycellulo-
ses: 1) unoxidized cellulose; 2) 4.5% COOH;
3) 6.5% COOH; 4) 9.0% COOH; 5) 10.5% COOH

Data on the Decarboxylation of Oxycelluloses and Products of Their Aqueous Hydrolysis

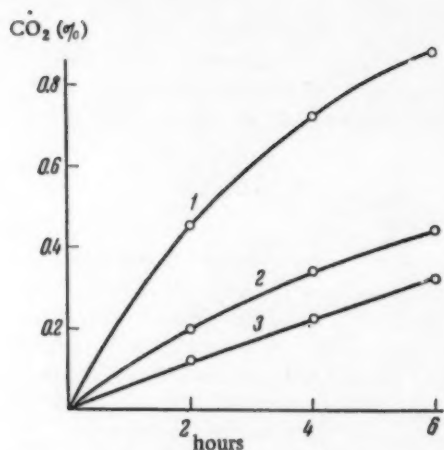| Method of determining COOH-groups	Dialdehydocellulose (6.4% CHO)			COOH (%) (Ac)$_2$ method)		
	original preparation	hydrolyzate	undissolved part	original preparation	hydrolyzate	undissolved part
% COOH (%) Ca (Ac)$_2$ method	0.41	—*	0.2	9.4	—*	1.8
% Uronic COOH (%)	0.44	0.9	0.32	0.83	1.66	0.32
CO$_2$ (mg)	8.34	5.5	3.13	15.47	11.01	4.23

Fig. 3. Decarboxylation of dialdehydo-cellulose (6.4% CHO) and products of its aqueous hydrolysis: 1) hydrolyzate; 2) original sample; 3) undissolved part.
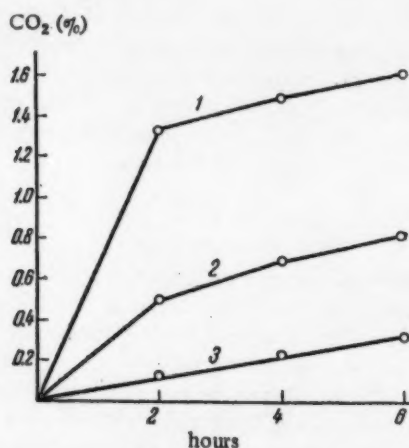
Fig. 4. Decarboxylation of dicarboxycellu-lose (9.4% COOH) and products of its aqueous hydrolysis: 1) hydrolyzate; 2) original sample; 3) undissolved part.

From a comparison of data on decarboxylation it will be seen that dicarboxycellulose yields almost twice as much CO$_2$ as the dialdehydocellulose from which it was obtained. This fact points to the presence of 6-alde-hyde groups in the dialdehydocellulose. Treatment of cellulose with sodium chlorite does not result in the liberation of more CO$_2$ than that given by the original cellulose (0.15%). It will be seen from Figures 3 and 4 that the curves for the hydrolyzates have well-marked characteristics of the curve for the decarboxylation of uronic acids. Nonuronic structures formed in the acid hydrolysis of celluloses under conditions of Tollens de-carboxylation (glyoxylic and tartaric acids, and also glucose and cellobiose) yield CO$_2$. As the amount of CO$_2$ liberated from such structures is insignificant and their decarboxylation curves are linear [14, 15], this fact can-not have any substantial effect on our results. Hence, the oxidation of cellulose with sodium periodate with subsequent oxidation with sodium chlorite can be represented by the following scheme:

The structures (VI) and (VII) can also be formed by the action of $NaIO_4$ and $NaClO_2$, but the establishment of their presence requires a special investigation. Oxidation at the 6-carbon atom under the action of $NaIO_4$ and $NaClO_2$ proceeds on the average to the extent of about 10%, as compared with the main direction of the oxidation reaction.
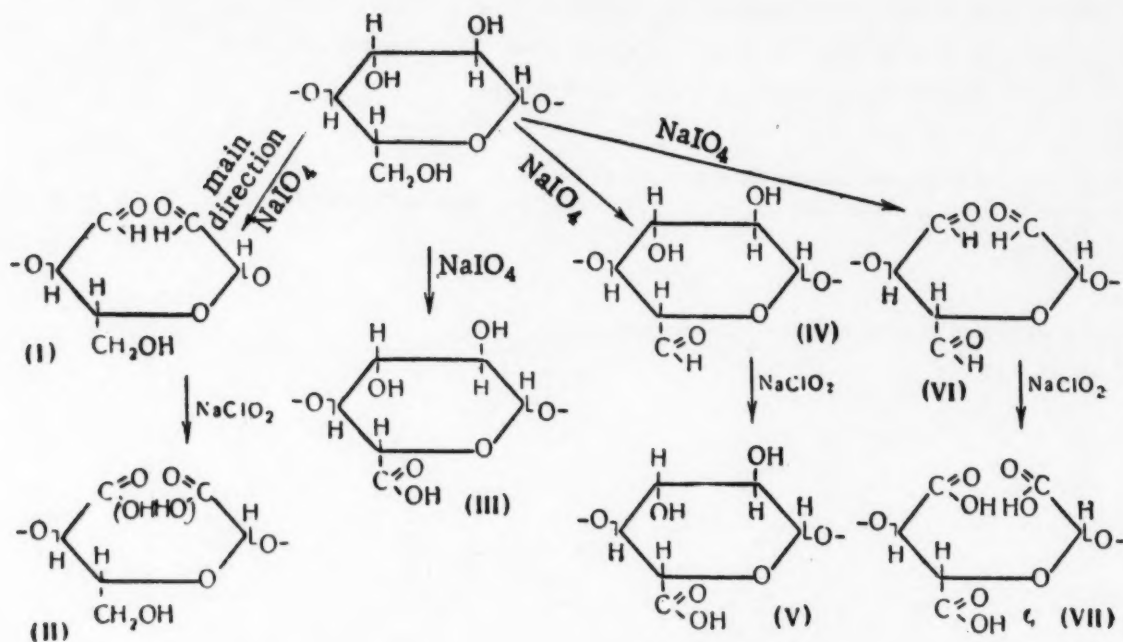
SUMMARY

Sodium periodate oxidizes not only the α-glycol grouping, but also the alcohol group in the 6-position of cellulose, to aldehyde and carboxy groups.

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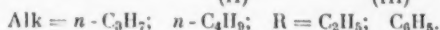N. D. Zelinskii Institute of Organic Chemistry of the
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*Original Russian pagination. See C. B. Translation.

ACTION OF PRIMARY AMINES ON ALKANECHLOROBORONIC ESTERS

B. M. Mikhailov and T. A. Shchegoleva

One of us and Kostroma [1] showed that primary and secondary aliphatic amines react with arenechloroboronic esters with formation of N-alkyl- and N, N-dialkyl-areneamidoboronic esters ArBNHR(OR') and ArBNR$_2$-
-(OR'). In the present investigation we have studied the action of primary amines (ethylamine and aniline) on alkanechloroboronic esters. It might be expected, on analogy to the behavior of arenechloroboronic esters, that reaction with ethylamine would yield N-ethyl-alkanechloroboronic esters (I, R = C$_2$H$_5$), but only the products of the symmetrization of these compounds were isolated, namely N,N'-diethylalkaneboronamides (II, R = C$_2$H$_5$) and alkaneboronic esters (III). Alkanechloroboronic esters react similarly toward aniline with formation of a mixture of N,N'-diphenylalkaneboronamides (II, R = C$_6$H$_5$) and alkaneboronic esters (III). These reactions evidently proceed according to the following equations:

$$AlkBCl(OC_4H_9) + 2RNH_2 \rightarrow AlkBNHR(OC_4H_9) + RNH_2 \cdot HCl$$
$$(I)$$
$$2AlkBNHR(OC_4H_9) \rightarrow AlkB(NHR)_2 + AlkB(OC_4H_9)_2$$
$$(II) \qquad\qquad (III)$$
$$Alk = n\text{-}C_3H_7; \quad n\text{-}C_4H_9; \quad R = C_2H_5; \quad C_6H_5.$$

Thus, by the action of ethylamine on propane- and butane-chloroboronic esters we obtained N, N'-diethyl-propane- and N,N'-diphenylbutane-boronamides. These substances are the first organoboron compounds to be prepared in which boron is attached simultaneously to an alkyl group and two alkyl- or aryl-amino groups.

Alkaneboronamides of type (II) change rapidly in the air and are readily hydrolyzed with water. They are converted by alcohols into alkaneboronic esters and the corresponding amines. If an equimolecular amount of alcohol is used, only one-half of the diamide (II) reacts. The reaction clearly proceeds through the stage of the amido ester (IV), which is then either symmetrized into the ester and the original diamide or attacked by a second alcohol molecule:

$$n\text{-}C_4H_9B(NHC_2H_5)_2 + ROH \rightarrow [n\text{-}C_4H_9BNHC_2H_5(OR)]$$
$$\downarrow \quad\quad ROH \qquad (IV)$$
$$n\text{-}C_4H_9B(NHC_2H_5)_2 + n\text{-}C_4H_9B(OR)_2 \quad \text{or} \quad n\text{-}C_4H_9B(OR)_2 + C_2H_5NH_2$$

EXPERIMENTAL

All operations with organoboron compounds were carried out in an atmosphere of nitrogen.

Action of Ethylamine on Butyl Propanechloroboronate. A solution of 22.2 g (0.5 mole) of ethylamine in 50 ml of dry ether was cooled to −70° and stirred while a solution of 40 g (0.25 mole) of butyl propanechloroboronate in 50 ml of ether was added over a period of two hours. The reaction mixture, which contained a white amorphous precipitate, was stirred for 30 minutes with cooling and then warmed to room temperature. The amorphous gel-like precipitate became crystalline; it was filtered off and washed with ether (21 g). It was ethylamine hydrochloride, m.p. 108-110°.

Ether was distilled from the filtrate. Fractional distillation of the residue gave:

1) 8.2 g (46%) of N,N'-diethylpropaneboronamide, b.p. 50-51° (7 mm); d^{20}_4 0.7927; n^{20}_4 1.4230; MR 45.64.

Found %: C 59.13; H 13.65; B 7.52 $C_7H_{19}BN_2$. Calculated %: C 59.24; H 13.49, B 7.62.

2) 18.6 g (74%) of dibutyl propaneboronate, b.p. 65-68° (2 mm) and $n^{20}D$ 1.4120.

3) 3.1 g of a fraction of b.p. 68-100° (2 mm).

Action of Ethylamine on Butyl Butanechloroboronate. For reaction we took 27.2 g (0.6 mole) of ethylamine in 50 ml of ether and 53 g (0.3 mole) of butyl butanechloroboronate in 50 ml of ether. The experiment was carried out analogously to the preceding one. We obtained 24 g of ethylamine hydrochloride, m.p. 106-108°.

Fractional distillation of the liquid reaction products gave:

1) 11.0 g (50%) of N,N'-diethylbutaneboronamide, b.p. 55-60° (4 mm); after redistillation it had b.p. 55-56° (4 mm); d^{20}_4 0.7965; $n^{20}D$ 1.4283; MR 50.46.

Found %: C 61.80; H 13.53; B 6.84; N 18.05 $C_8H_{21}BN_2$. Calculated %: C 61.55; H 13.56; B 6.93; N 17.91.

2) 25.6 g (80%) of dibutyl butaneboronate, b.p. 83-87° (4 mm) and $n^{20}D$ 1.4153.

3) 3.2 g of a substance of b.p. 129-134° (3 mm), the analysis of which corresponded to $C_{10}H_{23}BNO$.

Found %: C 60.35; H 11.51; B 11.27; N 7.30 $C_{10}H_{23}B_2NO$. Calculated %: C 61.61; H 11.89; B 11.10; N 7.19.

Action of Aniline on Butyl Propanechloroboronate. A solution of 32.8 g (0.2 mole) of butyl propanechloroboronate in 50 ml of dry ether was added over a period of two hours at room temperature to a solution of 37.5 g (0.4 mole) of aniline in 50 ml of ether. The temperature of the reaction mixture rose slightly, and a colorless crystalline precipitate formed. The mixture was stirred for 90 minutes, and the precipitate was filtered off and washed with ether (28.2 g). It was aniline hydrochloride, m.p. 196-197.5°. Solvent was distilled from the filtrate, and fractional distillation of the residue gave:

1) 14.7 g (73%) of dibutyl propaneboronate, b.p. 65-67° (2 mm) and $n^{20}D$ 1.4115.

2) 13.5 g (58%) of N,N'-diphenylpropaneboronamide; b.p. 122-125° (0.1 mm); d^{20}_4 1.0187; $n^{20}D$ 1.5820; MR 78.02.

Found %: C 75.67; H 8.08 B 4.54; $C_{15}H_{19}BN_2$. Calculated %: C 75.68; H 8.03; B 4.53.

Action of Aniline on Butyl Butanechloroboronate. For reaction we took 37.2 g (0.4 mole) of aniline in 50 ml of ether and 35.3 g (0.2 mole) of butyl butanechloroboronate in 50 ml of ether. The procedure was as in the preceding experiment. We obtained 28.4 g of aniline hydrochloride, m.p. 193-194°. Distillation of the liquid products gave:

1) 18.1 g (84%) of dibutyl butaneboronate, b.p. 85-86° (3 mm) and $n^{20}D$ 1.4150.

2) 16.9 g (70%) of N,N'-diphenylbutaneboronamide; b.p. 136-138° (0.2 mm); d^{20}_4 1.0078; $n^{20}D$ 1.5757; MR 82.77.

Found %: C 76.25; H 8.46; B 4.42 $C_{16}H_{21}BN_2$. Calculated %: C 76.20; H 8.40; B 4.29.

Action of Butyl Alcohol on N,N'-Diethylbutaneboronamide. To 8.6 g (0.055 mole) of N,N'-diethylbutaneboronamide we added 4.1 g (0.055 mole) of butyl alcohol. The butyl alcohol dissolved immediately, and the temperature of the mixture rose slightly. After one hour the reaction mixture was fractionally distilled, and we collected Fraction I (2.8 g), b.p. 56-60° (2 mm), and Fraction II (5.6 g), b.p. 72-77° (2 mm). Fraction I was found to be N,N'-diethylbutaneboronamide (33% of the amount taken for reaction) having $n^{20}D$ 1.4293. Fraction II was dibutyl butaneboronate (yield 98%) having $n^{20}D$ 1.4155.

Action of Methanol on N,N'-Diethylbutaneboronamide. To 9.6 g (0.06 mole) of N,N'-diethylbutaneboronamide we added 2 g (0.06 mole) of absolute methanol. The alcohol dissolved immediately, and the temperature of the mixture rose slightly. After one hour the reaction mixture was fractionally distilled, and we collected Fraction I (2.5 g), b.p. 37-38° (21 mm), and Fraction II (4.1 g), b.p. 62-65° (4 mm). Fraction I was found to be dimethyl butaneboronate (yield 73.4%); d^{20}_4 0.8372; $n^{20}D$ 1.3933; MR 37.10.

Found %: C 55.36; H 11.60; B 8.47 $C_6H_{15}BO_2$. Calculated %: C 55.43; H 11.63; B 8.32.

Fraction II was unchanged N, N'-diethylbutaneboronamide (43% on the amount taken for reaction).

SUMMARY

By the action of primary amines, alkanechloroboronic esters were converted into alkaneboronic esters and N,N'-dialkylalkaneboronamides.

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*Original Russian pagination. See C.B. Translation.

SYNTHESIS OF TETRAKIS(TRIETHYLSILOXY)TITANIUM AND TETRAKIS(TRIETHYLSILOXY)TIN

K. A. Andrianov and A. A. Zhdanov

A few papers have appeared on the synthesis of organosilicon derivatives of titanium [1-3]. Organosilicon polymers containing the Si − O − Sn linkage have been described [4]. Our investigations showed that the method developed by us earlier [5] for the synthesis of tetrakis(trimethylsiloxy)titanium by reaction of sodium trimethylsiloxide with titanium tetrachloride,

$$4\,(C_2H_5)_3SiONa + TiCl_4 \rightarrow [(C_2H_5)_3SiO]_4Ti + 4NaCl$$
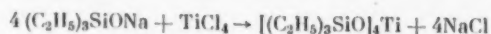
can be successfully used for the preparation of tetrakis(triethylsiloxy)titanium. Investigation of this reaction led to the synthesis of a new, monomeric compound containing an Si − O− Sn linkage, tetrakis(triethylsiloxy)tin:

$$4(C_2H_5)_3SiONa + SnCl_4 \rightarrow [(C_2H_5)_3SiO]_4Sn + 4NaCl.$$
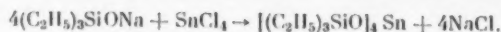
The investigation of this reaction and also of the reaction of sodium triethylsiloxide with other halides will be reported in detail in the near future.

EXPERIMENTAL

Tetrakis(triethylsiloxy)titanium. A solution of 26.6 g (0.14 mole) of titanium tetrachloride in 100 ml of benzene was added dropwise to a solution of 86.2 g (0.56 mole) of sodium triethylsiloxide in 200 ml of benzene contained in a three-necked flask fitted with stirrer, dropping funnel, and thermometer. In the course of the addition of titanium tetrachloride the temperature rose to 80°. When the addition was complete, the mixture was stirred further for 15 minutes, after which the precipitate was filtered off. Benzene was distilled from the filtrate. Vacuum fractionation of the residue gave 45 g (56.1%) of a crystalline solid; b.p. 221-222° (9 mm); m.p. 96°.

Found %: C 50.61; 50.48; H 10.74; 10.63; Si 18.92; 18.80; Ti 9.05; 9.08 $C_{24}H_{60}O_4Si_4Ti$. Calculated %: C 50.32; H 10.56; Si 19.59; Ti 8.36.

Tetrakis(triethylsiloxy)tin. The procedure was similar. We took 61.5 g (0.4 mole) of sodium triethylsiloxide in 75 ml of benzene and 26.1 g (0.1 mole) of stannic chloride in 200 ml of benzene. During the addition of the stannic chloride the temperature rose to 40°. Solvent was distilled off, and fractionation of the residue gave 34.5 g (53.7%) of a substance of b.p. 200-202° (4 mm).

Found %: C 44.90; 44.80; H 9.67; 9.56; Si 17.01; 16.98; Sn 19.52; 19.43 $C_{24}H_{60}O_4Si_4Sn$. Calculated %: C 44.78; H 9.39; Si 17.44, Sn 18.44.

SUMMARY

By the metathetic reaction of sodium triethylsiloxide with titanium tetrachloride and with tin tetrachloride, tetrakis(triethylsiloxy)titanium and tetrakis(triethylsiloxy)tin were synthesized.

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SYNTHESIS OF 2-CYCLOHEXYLBICYCLOPROPYL

A. P. Meshcheriakov and V. G. Glukhovtsev

Up to now only four hydrocarbons are known with two cyclopropane rings in their molecules: spiropentane [1], bicylopropyl [2], dicyclopropylmethane [3], and 2-phenylbicyclopropyl [4].

With the object of studying the properties of such hydrocarbons we synthesized 2-cyclohexylbicyclopropyl as follows:
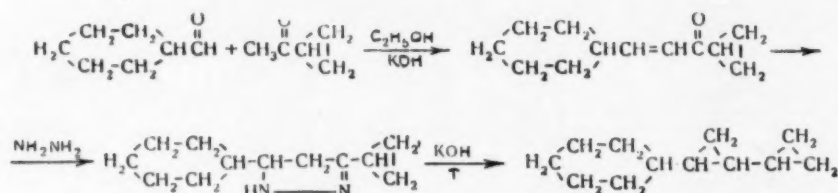
Also, we made an attempt to prepare 2-hexylbicyclopropyl under similar conditions from heptanal and cyclopropyl methyl ketone. However, instead of cyclopropyl 1-octenyl ketone we obtained 8-tetradecen-7-one. From 8-tetradecen-7-one and hydrazine hydrate we obtained a mixture of the hydrazone and the pyrazoline base, which, when decomposed over potassium hydroxide, gave a mixture of 6-tetradecene and 1-hexyl-2-pentylcyclopropane. Hence, under these conditions cyclopropyl methyl ketone condenses with an aromatic aldehyde [4], with a cyclohexanecarboxyaldehyde, but not with an aliphatic aldehyde which also has seven carbon atoms in its molecule.

In view of this it was necessary to study the tendency for cyclopropyl methyl ketone to condense with itself under the influence of various catalysts. It was shown that cyclopropyl methyl ketone does not condense at 20° in the course of 16 days in presence of alcoholic KOH, C_2H_5ONa, or Ba (OH)$_2$. When treated with sodium, cyclopropyl methyl ketone formed a mixture of b.p. 140-250° (3 mm).

According to Bunce [5], cyclopropyl methyl ketone, treated with tert-butylmagnesium chloride, gives a low yield of a product which consists mainly of 1,3-dicyclopropyl-2-buten-1-one, but contains also 2-cyclopropyl-3,3-dimethyl-2-butanol (9% yield). In this case we succeeded in isolating only the latter (19% yield). When cyclopropyl methyl ketone was boiled with potassium hydroxide, we obtained 1,3,5-tricyclopropyl-3,5-epoxy-1-hexanone, formed as follows:
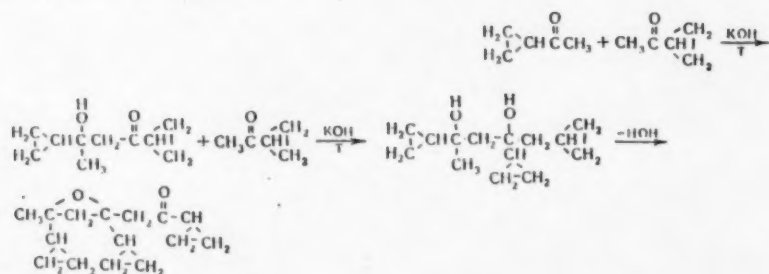
5-Chloro-2-pentanone $CH_3COCH_2CH_2CH_2Cl$. 5-Hydroxy-2-pentanone (306 g; b.p. 99.5° / 12 mm) was cooled to 0° and added with stirring over a period of two hours to 650 ml of hydrochloric acid which had been saturated with HCl under cooling until the density reached 1.22. The mixture was stirred for 10 hours and then poured into three times its volume of water. The mixture was extracted with ether, and the ether extract was dried with calcium chloride. After removal of ether we obtained 230 g of 5-chloro-2-pentanone; b.p. 74° (21 mm); $n^{20}D$ 1.4376; d^{20}_4 1.0517; found MR 30.07; calculated MR 30.12; yield 64%.

When the 5-hydroxy-2-pentanone was saturated with HCl or treated with $SOCl_2$ the yield of 5-chloro-2-pentanone was reduced to 25%.

Cyclopropyl methyl ketone. This was prepared from 5-chloro-2-pentanone and potassium hydroxide in 76% yield by the method given in [6]; b.p. 111.5° (757 mm); $n^{20}D$ 1.4240; d^{20}_4 0.9001; found MR 23.84; calculated MR 23.15.

Cyclohexanecarboxaldehyde. This was prepared from ethyl chloroacetate and cyclohexanone by the procedure given in [7] via ethyl 1-oxaspiro [2.5] octane-2-carboxylate (b.p. 123° (11 mm); $n^{20}D$ 1.4584; d^{20}_4 1.0524; found MR 47.80; calculated MR 47.21), and further via hydroxycyclohexanecarboxylic acid, in 50% yield. Cyclohexanecarboxaldehyde had b.p. 75° (20 mm); $n^{20}D$ 1.4510; d^{20}_4 0.9350; found MR 32.3; calculated MR 32.41.
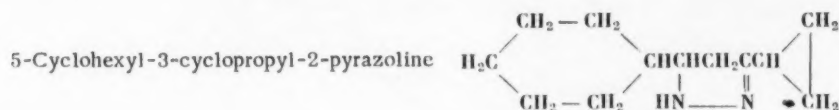
3-Cyclohexyl-1-cyclopropyl-2-propen-1-one
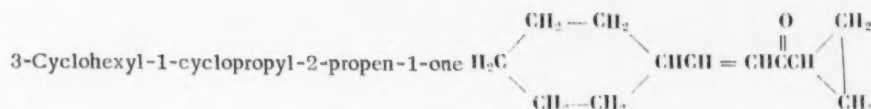
Alcoholic potassium hydroxide (6 g of KOH in 180 ml of C_2H_5OH) was added over a period of two hours to a stirred, cooled mixture of 112 g of cyclohexanecarboxaldehyde and 90 g of cyclopropyl methyl ketone. Stirring continued for five hours at 20°. The contents of the flask were then poured into water and extracted with ether. Ether was distilled off, and the residue was vacuum-distilled. We obtained 107 g (60%) of 3-cyclohexyl-1-cyclopropyl-2-propen-1-one; b.p. 112-114° (2 mm); $n^{20}D$ 1.4995; d^{20}_4 0.9649; found MR 54.29; calculated MR 52.96.

Found %: C 80.34; 80.37; H 10.14; 10.10 $C_{12}H_{18}O$. Calculated %: C 80.84; H 10.17.

The semicarbazone had m.p. 141-142°.

Found %: N 18.07; 17.85 $C_{13}H_{21}N_3O$. Calculated %: N 17.87

5-Cyclohexyl-3-cyclopropyl-2-pyrazoline

A solution of 28 ml of hydrazine hydrate in 20 ml of ethanol was added to 50 g of 3-cyclohexyl-1-cyclopropyl--2-propen-1-one in 50 ml of ethanol. The mixture was then heated at 80-90° for eight hours. Alcohol and hydrazine hydrate were distilled off, and we obtained 35 g of the pyrazoline base; b.p. 145-147° (2 mm); $n^{20}D$ 1.5157; d^{20}_4 1.0045; found MR 57.79; calculated MR 57.56. On standing, the base solidified; m.p. 40-75°. The product was not analyzed because of its instability. In addition we isolated 13.5 g of a product of b.p. 212-214° (2 mm), probably 3-cyclohexyl-1-cyclopropyl-2-propen-1-one azine; $n^{20}D$ 1.5330; d^{20}_4 1.0016; found MR 109.24; calculated MR 110.22; yield 25%.

Found % C 80.46; 80.31; H 10.17; 10.15; N 7.70; 7.69 $C_{24}H_{36}N_2$. Calculated %: C 81.75; H 10.29; 7.94.

2-Cyclohexylbicyclopropyl
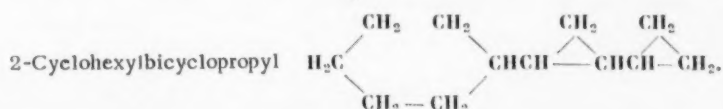
This was prepared by the decomposition of 5-cyclohexyl-3-cyclopropyl-2-pyrazoline in presence of potassium hydroxide. The 5-cyclohexyl-3-cyclopropyl-2-pyrazoline (42 g) was slowly distilled over potassium hydroxide powder up to 218°. The hydrocarbon layer was separated from the aqueous layer, washed three times with 50% acetic acid (10-ml portions), neutralized with potassium carbonate, and dried over potassium hydroxide. After one distillation in absence of sodium and six distillations over sodium we obtained 19.5 g (54.5%) of 2-cyclohexylbicyclopropyl; b.p. 82° (3 mm); $n^{20}D$ 1.4720; d^{20}_4 0.8785; found MR 52.36; calculated MR 51.30. Yield 54.5%.

Found %: C 86.92; 87.16; H 12.04; 12.12 $C_{12}H_{20}$. Calculated %: C 87.72; H 12.27.

By the condensation of cyclopropyl methyl ketone with heptanal we isolated, in more than 80% yield, 8-tetradecen-7-one, which was not distilled because of its instability; $n^{20}D$ 1.4606; d^{20}_4 0.8598; found MR 67.07; calculated MR 66.48.

Found %: C 79.27; 79.10; H 12.12; 12.18 $C_{14}H_{26}O$. Calculated %: C 79.93; H 12.45.

By reaction of 8-tetradecen-7-one with hydrazine hydrate and decomposition of the product over potassium hydroxide we obtained, after careful purification, a product of b.p. 118° (8 mm); $n^{20}D$ 1.4405; d^{20}_4 0.7757; found MR 66.78; calculated MR 66.48.

Found %: C 85.70; 85.75; H 14.04; 14.23 $C_{14}H_{28}$. Calculated %: C 85.62; H 14.37.

According to analysis by Raman spectra, the product was 6-tetradecene with some admixture of 1-hexyl--2-pentylcyclopropane.

Condensation of Cyclopropyl Methyl Ketone in Presence of Potassium Hydroxide. A mixture of 140 g of cyclopropyl methyl ketone and 15 g of potassium hydroxide powder was boiled for eight hours. The temperature of the mixture rose from 111° to 180°. When 60 g of cyclopropyl methyl ketone had been distilled off, we isolated 29 g of a product of b.p. 156-157° (3 mm); $n^{20}D$ 1.4960; d^{20}_4 1.0215; found MR 67.01; calculated MR 64.83. calculated (with correction for three rings) MR 66.93.

Found %: C 77.20; 77.09; H 9.46; 9.40 $C_{15}H_{22}O_2$. Calculated %: C 76.88; H 9.46.

There were no double bonds or active hydrogen in this compound. It was probably 1,3,5-tricyclopropyl--3,5-epoxy-1-hexanone. The condensation was slower when sodium hydroxide was used.

Reaction of Cyclopropyl Methyl Ketone with tert-Butylmagnesium Chloride. Cyclopropyl methyl ketone (31 g) was added to a Grignard reagent prepared from 12.2 g of magnesium and 58 g of tert-butyl chloride in 200 ml of ether. After the usual treatment we obtained 10 g (19%) of 2-cyclopropyl-3,3-dimethyl-2-butanol; b.p. 172.5° (761 mm); $n^{20}D$ 1.4470; d^{20}_4 0.8807; found MR 43.14; calculated MR 43.40

Found %: C 76.29; 76.30; H 12.75; 12.64 $C_9H_{18}O$. Calculated %: C 76.00; H 12.75.

Found %: H_{active} 0.66; 0.73; 0.63; 0.63 $C_9H_{18}O$. Calculated %: H_{active} 0.70.

SUMMARY

1. 2-Cyclohexylbicylopropyl was synthesized, and its physicochemical properties were determined.

2. A method was developed for the preparation of 5-chloro-2-pentanone from 4-hydroxy-2-pentanone and hydrochloric acid.

3. The condensation of cyclopropyl methyl ketone in presence of catalysts (alcoholic KOH, C_2H_5ONa, $Ba(OH)_2$, Na, NaOH, KOH) was studied. 1,3,5-tricyclopropyl-3,5-epoxy-1-hexanone was prepared.

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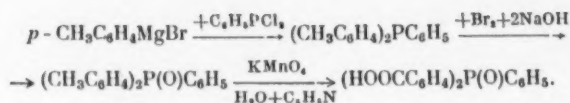
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SOME PHOSPHORUS-CONTAINING POLYAMIDES

T. M. Frunze, V. V. Korshak, V. V. Kurashev, G. S. Kolesnikov,
and B. A. Zhubanov

With the object of determining the effect of the presence of a phosphorus atom on the properties of poly-amides we prepared a series of polymers by the polycondensation of p,p'-(phenylphosphinylidene)dibenzoic acid (bis (p-carboxyphenyl)phenylphosphine oxide) with various aliphatic and aromatic diamines. We prepared the dibasic acid as follows:

$$p - CH_3C_6H_4MgBr \xrightarrow{+C_6H_5PCl_2} (CH_3C_6H_4)_2PC_6H_5 \xrightarrow{+Br_2+2NaOH}$$

$$\rightarrow (CH_3C_6H_4)_2P(O)C_6H_5 \xrightarrow[H_2O+C_5H_5N]{KMnO_4} (HOOCC_6H_4)_2P(O)C_6H_5.$$

The polycondensation was carried out under the usual conditions [1] with gradual rise of temperature to 260°. In the polycondensation of p,p'-(phenylphosphinylidene)dibenzoic acid with aliphatic diamines the start-ing materials were the salts formed by the reactants (Table 2), which were pale-yellow powders, soluble in water, methanol, and ethanol, but insoluble in ether, acetone, and benzene. In the case of the aromatic diamines, which, being weak bases, do not form salts with organic acids, in the reaction we took stoichiometric amounts of the acid and diamine together with a slight excess (about 5%) of the latter. The properties of the polyamides obtained are given in Table 1. The polyamides were slightly colored, noninflammable, clear substances, soluble in cresol and formic and acetic acids.

From the results it will be seen that with increase in the chain length of the diamine from four carbons to ten the softening and flow points of the polyamides fall. The same is observed also in the case of the usual polyamides and is associated with change in the number of hydrogen bonds formed between macromolecules arising from the reduction in the relative number of amide groupings [2]. Phosphorus-containing polyamides containing aromatic diamine residues melt higher than those derived from aliphatic diamines, clearly as a result of the more rigid structure of the macromolecule.

The effect of isomerism in the diamine residue is the same here as in the case of the usual polyamides: with reduction in the symmetry (with passage from p- to o- and m-phenylenediamines), the softening and flow points are lowered [3]. The introduction of a substitutent into the nucleus of a diamine (toluene-2,4-diamine) results in lower softening and flow points, as compared with the corresponding unsubstituted diamines.

EXPERIMENTAL

Synthesis of Phenyldi-p-tolylphosphine. A solution of 100 g (0.57 mole) of dichlorophenylphosphine in 100 ml of ether was added dropwise with stirring to the organomagnesium compound prepared by reaction of 190.5 g (1.14 moles) of p-bromotoluene with 27.7 g (1.14 g-atoms) of magnesium in 300 ml of ether. When the addition was complete, the mixture was boiled for two hours; it was then decomposed with water. The two layers, ethereal and aqueous, were separated. The aqueous layer was extracted several times with ether. The ethereal solutions were combined and dried with magnesium sulfate; ether was distilled off, and the residue was vacuum-distilled with collection of the fraction of b.p. 140-145° (2 mm). The yield of phenyldi-p-tolyl-phosphine was 40% on the amount of p-bromotoluene taken; m.p. 53-54° (the literature [4] gives 56-57°).

TABLE 1

Properties of Polyamides Prepared from p,p'-(Phenylphosphinyl-idene)dibenzoic Acid and Diamines of the Aliphatic and Aromatic Series

Diamine	Temperature (°C) of		Reduced viscosity $[\eta_{sp}/c]_{c=0.5}$
	start of softening*	flow**	
1,4-Butanediamine	180	204	0.18
1,6-Hexanediamine	180	190	0.42
1,10-Decanediamine	150	179	0.38
p-Phenylenediamine	260	Decomposes at 340	0.24
m-Phenylenediamine	249	Decomposes at 340	0.20
o-Phenylenediamine	168	184	0.08
Toluene-2,4-diamine	239	252	0.18

* Determined below a layer of paraffin [1].

** Results of thermomechanical investigation.

Synthesis of Phenyldi-p-tolylphosphine Oxide. The procedure described by Plets [5] for the preparation of triphenylphosphine oxide was used. The yield of phenyldi-p-tolylphosphine oxide was almost theoretical; m.p. 80-81° (the literature [6] gives 79-80°).

Synthesis of p,p'-(Phenylphosphinylidene)dibenzoic Acid. This was carried out by the oxidation of phenyl-di-p-tolylphosphine oxide with potassium permanganate in an aqueous pyridine medium by the method of Morgan and Herr [6]. The dicarboxylic acid isolated had m.p. 340-342°.

Found %: C 65.22; 66.00; H 4.26; 4.38; P 8.37; 8.04 $C_{20}H_{15}O_5P$. Calculated %: C 65.49; H 4.11; P 8.45.

TABLE 2

Aliphatic Diamine Salts of p,p'-(Phenylphosphinylidene)dibenzoic Acid

Diamine	M.p. (°C)	Found (%)				Calculated (%)			
		C	H	P	N	C	H	P	N
1,4-Butanediamine	239—240	59.41	6.33	5.99	7.05	61.02	6.18	6.55	5.97
		59.59	6.24	6.31	7.28				
M.p. (°C)	212—214	61.76	6.93	5.65	5.76	62.38	6.64	6.11	5.59
		62.19	6.92	5.71	5.61				
1,6-Hexanediamine	216—218	64.12	7.48	5.33	5.54	64.73	7.42	5.56	5.03
		64.02	7.26	5.60	5.50				

Preparation of the 1,10-Decanediamine Salt of p,p'-(phenylphosphinylidene)dibenzoic Acid. The salt was prepared from 3.40 g (0.095 mole) of the acid and 1.71 g (0.099 mole, a 5% excess) of 1,10-decanediamine in 15 ml of ethanol. The resulting pale-yellow viscous solution was filtered; the filtrate was washed with benzene, and the lower layer was separated and dried in a vacuum oven at 50°. In a similar way we prepared the 1,4-butanediamine and 1,6-hexanediamine salts. The characterization of the salts is given in Table 2.

SUMMARY

Polyamides derived from p,p'-(phenylphosphinylidene)dibenzoic Acid and some aliphatic and aromatic diamines were prepared and investigated.

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** In Russian.

ISOLATION OF CARBOHYDRATE-CONTAINING PEPTIDES FROM
FERMENTATION HYDROLYZATES OF EGG ALBUMIN

E. D. Kaberzneva and F. V. Shmakova

The question of the way in which carbohydrates are associated with proteins in the mucoids (which occur extensively in the living organism) and in other carbohydrate-protein complexes has not yet been resolved. There can be no doubt that this association may be effected in various ways; thus, in some proteins there are covalent links, and in others the carbohydrate complex is held together by ionic and hydrogen bonds, and even by adsorption forces. In 1938 Neuberger [1] showed conclusively that in egg albumin the polysaccharide is bound chemically and consists of two molecular proportions of glucosamine, four molecular proportions of mannose, and an unknown nitrogenous substance, the nature of which has not yet been elucidated. The method and point of attachment of the polysaccharide to the protein part of the molecule have not been studied.

We set ourselves the task of partially hydrolyzing egg albumin without splitting off the carbohydrate complex and of isolating the carbohydrate-containing fragments of the molecules (peptides) in order to make a study of them. For this purpose crystalline egg albumin was given a brief hydrolysis with crystalline pepsin, and also with crystalline trypsin. The resulting pepsin and trypsin hydrolyzates were subjected to prolonged fractionation. It was then found that peptides associated with carbohydrates were present mainly in fractions of basic and acid peptides, and to a lesser extent in the fraction of neutral peptides. From trypsin hydrolyzates, after separation of unchanged protein by dialysis, resolution of the hydrolyzate into three fractions by electrophoresis, fraction precipitation of each fraction with acetone, and isolation of carbohydrate-containing peptides by repeated chromatography on paper, we obtained peptide fractions that could be regarded as fairly pure individual compounds. This conclusion was based on the fact that these fractions were very constant and similar in amino-acid composition, in spite of difference in the technique of separation. In addition to amino acids these peptides contained glucosamine, mannose, and an unknown substance "X", which was revealed on chromatograms by the benzidine carbohydrate reaction after it had been oxidized with periodic acid, i.e., it contained a glycol grouping, but did not give carbohydrate reactions depending on the presence of an aldehyde group. This compound is probably the unidentified component of the carbohydrate complex noted by Neuberger, or a product of its decomposition.

The following table gives the compositions of the carbohydrate-containing peptides from egg albumin.

Notes. The following abbreviations are used: lysine, lys; leucine, leu; threonine, thre; glycine, gly; phenylalanine, phen; arginine, arg; glutamic acid, glu; alanine, ala; proline, pro; valine, val; glucosamine, gluc; mannose, man; "X" is an unknown compound giving a strong reaction for the glycol grouping, but not containing aldehyde groups.

As will be seen from the table, all the purified peptide fractions containing carbohydrates and the unknown compound X have the same constant set of five amino acids (or, in the case of the basic peptides, six amino acids). The fractions differ among themselves with respect to several nonconstant components. There is reason to suppose that these amino acids are components of the peptide part of the molecule with which the polysaccharide complex is associated in egg albumin.

TABLE

Method of isolation of peptides	Composition				
Basic-peptide fraction					
Fr. IV of acetone precipitation a) After one purification by paper chromatography	lys	arg, glu, ala, pro,val	leu, thre	X, gluc, man	
b) After three purifications by paper chromatography	lys	arg, glu, ala, pro, val	— — gly	X	
Basic-peptide fraction from extreme cathode chamber					
a) Carbohydrate zone I (two purifications by paper chromatography)	lys	arg, glu, ala, pro,val	leu, thre, gly	X	
b) Carbohydrate zone II (two purifications by paper chromatography)	lys	arg, glu, ala, pro, val	leu, thre, gly	— gluc, man	
Acidic-peptide fraction					
Fr. IV of acetone precipitation (two purifications by paper chromatography)	—	arg, glu, ala, pro, val	— thre, phen	X	

SUMMARY

Carbohydrate-containing peptides were found among the products of the enzymic breakdown of egg albumin. All these peptides contained a constant group of five amino acids (arginine, glutamic acid, alanine, proline, and valine), and in basic peptides lysine was present also.

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# SYNTHESIS OF VINYL- AND 2-HALOVINYL-SILANES

V. F. Mironov and A. D. Petrov

Agre [1] showed that $HSiCl_3$ reacts at $500-600°$ with trichloro- and dichloro-ethylenes with formation of (2,2-dichlorovinyl)- and (1-chlorovinyl)-trichlorosilanes, respectively, in high yield. We have already reported [2] that $RSiHCl_2$, in which R = CH_3 and C_2H_5, reacts similarly with trichloroethylene at $550-600°$:
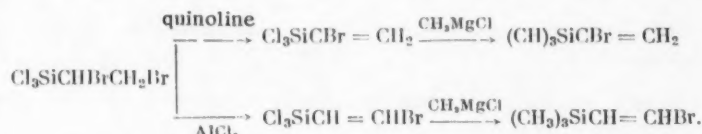
$$RCl_2SiH + Cl_2C = CHCl \xrightarrow{550°} RCl_2SiCH = CCl_2 + HCl.$$

The use of alkyldichlorosilanes in this reaction instead of $HSiCl_3$ has several advantages, both with respect to the accessibility of $RHSiCl_2$, and as a result of the suitability of the dichlorosilane obtained for use in the preparation of linear polysiloxanes.

In this paper we report the successful condensation of CH_3Cl_2SiH with vinyl chloride by passage of a mixture of the reactants through an empty tube heated to $550°$:

$$CH_3Cl_2SiH + ClCH = CH_2 \xrightarrow{550°} CH_3Cl_2SiCH = CH_2 + HCl.$$
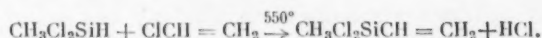
In this reaction the yield of dichloromethylvinylsilane attained 50%. High-temperature reaction between CH_3Cl_2SiH and cis-1,2-dichloroethylene under similar conditions gave a 20% yield of $ClCH = CHSiCH_3Cl_2$ and a considerable amount of $Cl_2CH_3SiCH = CHSiCH_3Cl_2$. The high-temperature condensation of CH_3Cl_2SiH with chlorotrifluoroethylene, allyl chloride, and 1-chloro-2-methylpropene also gives good yields of the corresponding alkenyldichloromethylsilanes. It should be noted that the multistage synthesis of these compounds by other known methods gives much lower yields, and the addition of $HSiCl_2CH_3$ to acetylene requires complicated apparatus [3]. The high-temperature condensation of CH_3HSiCl_2 with $BrCH = CHBr$ gives a complex mixture, and we did not succeed in isolating $BrCH = CHSiCl_2CH_3$. A compound of this type was obtained only by the elimination of HBr from $Cl_3SiCHBrCH_3Br$ with the aid of aluminum chloride.

We have already reported [4] that quinoline and aluminum chloride bring about the elimination of different chlorine atoms from $Cl_3SiCHClCH_2Cl$. The same behavior is again observed here:

$$Cl_3SiCHBrCH_2Br \begin{cases} \xrightarrow[\text{quinoline}]{} Cl_3SiCBr = CH_2 \xrightarrow{CH_3MgCl} (CH)_3SiCBr = CH_2 \\ \xrightarrow[AlCl_3]{} Cl_3SiCH = CHBr \xrightarrow{CH_3MgCl} (CH_3)_3SiCH = CHBr. \end{cases}$$

The synthesis of (2-bromovinyl)trimethylsilane in any other way is at present very difficult.

In conclusion we must point out that both (1-bromovinyl)- and (2-bromovinyl)-trimethylsilanes, unlike the corresponding chloro compounds, readily form reactive Grignard reagents in tetrahydrofuran. We shall shortly publish work on the synthesis of silylacrylic acids and other compounds with the aid of these reagents.

EXPERIMENTAL

Dichloromethylvinylsilane $CH_2 = CHSiCl_2CH_3$. A stream of vinyl chloride (17 liters/hour) was passed through an empty glass tube, diameter 20 mm and length 570 mm, heated to $550°$. Dichloromethylsilane (280 g) was passed into the same tube at the rate of one drop per second. The condensate, which was collected in a trap

cooled with ice, was distilled through a column and gave 143 g (41.5%) of dichloromethylvinylsilane, b.p. 92.5--93° and $n^{20}D$ 1.429 5.

Dichloro(2-chlorovinyl)methylsilane $ClCH = CHSiCl_2CH_3$ and 2,2,5,5-tetrachloro-2,5-disilahex-3-ene $CH_3Cl_2SiCH = CHSiCl_2CH_3$. A mixture of 225 g of dichloromethylsilane and 194 g of cis-1,2-dichloroethylene was passed through the same tube at the rate of one drop per second. Distillation through a column gave 75 g (21.4%) of $ClCH = CHSiCl_2CH_3$; b.p. 138-139°; $n^{20}D$ 1.4690; d^{20}_4 1.2629; found MR 38.71; calculated MR 38.34.

Found %: C 20.53; 20.43; H 2.91; 2.72; Si 16.50; 16.68 $C_3H_5SiCl_3$. Calculated %: C 20.51; H 2.87; Si 16.00.

In addition, a fraction of b.p. 196-197° and $n^{20}D$ 1.4805 was isolated, and in analysis and Raman spectrum this corresponded to $CH_3Cl_2SiCH = CHSiCl_2CH_3$. The residue in the still amounted to 6.3 g.

(2-Bromovinyl)trichlorosilane $BrCH = CHSiCl_3$. A mixture of 578 g of trichloro(1,2-dibromoethyl)silane [5] and 1 g of aluminum chloride was introduced into a flask fitted with a fractionation column. The contents of the flask were distilled over at 50 mm at about 70°. The condensate amounted to 461 g, and two fractionations of this through a column gave 33.4 g of a substance of b.p. 133-134°, $n^{20}D$ 1.4743; d^{20}_4 1.4355 and 124 g (28.7%) of $BrCH = CHSiCl_3$; b.p. 155-156°; $n^{20}D$ 1.5030; d^{20}_4 1.7207; found MR 41.30 calculated MR 40.73.

Found %: C 10.78; 10.86; H 1.03; 1.04; Si 11.76; 11.65 $C_2H_2SiBrCl_3$. Calculated %: C 9.99; H 0.84; Si 11.68.

(2-Bromovinyl)trimethylsilane $BrCH = CHSi(CH_3)_3$. (2-Bromovinyl)trichlorosilane (124 g) was added to CH_3MgCl prepared from 38 g of magnesium in 1 liter of ether. After a 10-hour boil the contents of the flask were decomposed with water. Ether was distilled off, and vacuum distillation of the residue gave 39 g (42%) of (2-bromovinyl)trimethylsilane; b.p. 44° (18 mm); $n^{20}D$ 1.4675; d^{20}_4 1.1628; found MR 42.32; calculated MR 42.12.

Found %: Si 15.67; 15.47 $C_5H_{11}SiBr$. Calculated % Si 15.67

$$\overset{\displaystyle Br}{\underset{|}{}}$$

(1-Bromovinyl)trimethylsilane $CH_2 = CSi(CH_3)_3$. (1-Bromovinyl)trichlorosilane [5] (98 g; b.p. 145.5°; $n^{20}D$ 1.4928; d^{20}_4 1.7151) was added to methylmagnesium iodide prepared from 35 g of magnesium and 210 g of methyl iodide in 700 ml of ether. The usual treatment gave 54 g (74%) of (1-bromovinyl)trimethylsilane; b.p. 47-48° (41 mm); $n^{20}D$ 1.4580; d^{20}_4 1.1562; found MR 42.28; calculated MR 42.12.

Found %: C 33.88; 33.82; H 6.18; 6.39; Si 15.67; 15.47 $C_5H_{11}SiBr$. Calculated %: C 33.52; H 6.18; Si 15.67.

SUMMARY

1. A method was developed for the synthesis in good yield and in simple apparatus of dichloromethyl-vinyl- and dichloro(2-chlorovinyl)methyl-silanes by the high-temperature condensation of CH_3SiHCl_2 with vinyl chloride and with cis-1,2-dichloroethane respectively.

2. In the dehydrobromination of $Cl_3SiCHBrCH_2Br$, quinoline eliminates the β-bromine atom and aluminum chloride the α-bromine atom.

3. (1-Bromovinyl)- and (2-bromovinyl)-trimethylsilanes form reactive Grignard reagents in tetrahydrofuran.

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PREPARATION OF N-OXIDES OF N-METHYLANABASINE

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In the development of our work on the N-oxides of tertiary-tertiary diacid bases [1,2] we carried out the oxidation of a close analog of nicotine, N-methylanabasine (1-methyl-2-(3-pyridyl)piperidine), with hydrogen peroxide and obtained all possible N-oxides of this compound (I, II, and III).

These compounds were characterized in the form of bases, picrates, and hydrochlorides. When the N-oxides were reduced with zinc in an acid medium, in all cases N-methylanabasine was obtained in good yield and was identified as the picrate. This reaction and the methods by which the N-oxides were prepared prove the structures of the N-oxides of N-methylanabasine beyond doubt and show that an unopened piperidine ring is present in these compounds.
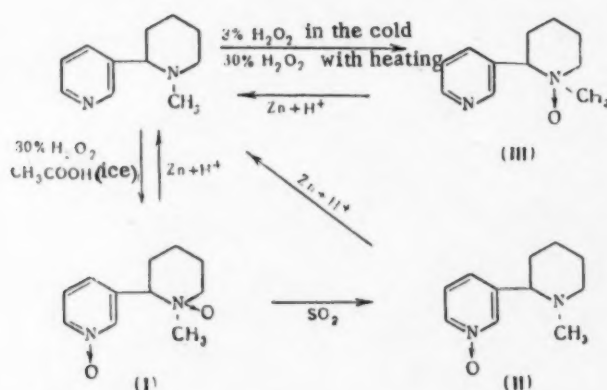
Preliminary experiments which we carried out with the object of oxidizing unalkylated anabasine showed that in this case, as would be expected from the work of Wolffenstein [3], oxidation is accompanied by opening of the piperidine ring. In the reaction mixture we found three products of an acidic character, and we are at present trying to determine their precise structures.

EXPERIMENTAL

N-Methylanabasine N,N'-Dioxide. A solution of 25 g of N-methylanabasine in a mixture of 600 ml of glacial acetic acid and 100 ml of 28.8% hydrogen peroxide was heated at 50-60° for 17 hours. Solvent was distilled off at 70° under reduced pressure. The residue, a viscous, almost colorless oil, was treated twice with 50 ml of water and twice with 50 ml of alcohol (in each case with subsequent removal of solvent by vacuum distillation); it was then dissolved in 50 ml of absolute alcohol and converted into its hydrochloride.

The dihydrochloride of N-methylanabasine N,N'-dioxide was prepared in square tablet-like crystals (very hygroscopic; decomposing at 200-204°) by adding alcohol saturated with HCl to a cooled solution of the base. Yield 30 g (75%); pH = about 4.5. The mother liquor gave a noncrystallizing oil.

Found %: C 46.68; 46.78; H 6.52; 6.34; N 9.74; 9.57 $C_{11}H_{18}N_2O_2Cl_2$. Calculated %: C 46.98; H 6.45; N 9.96.

The monopicrate of N-methylanabasine N,N'-dioxide was precipitated by picric acid from the aqueous solution of the reaction product, taken directly after distillation of solvent; m.p. 225-226° (with decomposition); crystallizes from water in yellow needles.

Found %: C 46.80; 46.85; H 4.28; 4.20 $C_{17}H_{19}N_5O_9$. Calculated %: C 46.86; H 4.38.

The same picrate was prepared from the hydrochloride.

Free base. A solution of 17 g of N-methylanabasine N,N'-dioxide dihydrochloride in 20 ml of water was treated with potassium carbonate. The liberated base was extracted with isobutyl alcohol, the extract was dried with calcined potassium carbonate, and solvent was distilled off. This gave 8.30 g (66%) of slightly colored solid base; after treatment with acetone it formed colorless hygroscopic crystals, m.p. 211°; pH = about 6.5.

Found %: C 62.48; 62.73; H 7.59; 7.67; N 13.68 $C_{11}H_{16}N_2O_2$. Calculated %: C 63.43; H 7.74; N 13.45.

Reduction of N-Methylanabasine N,N'-Dioxide. N-Methylanabasine N,N'-dioxide dihydrochloride (1 g) was reduced with zinc dust in 12% hydrochloric acid. The solution was made alkaline under cooling by the addition of sodium hydroxide powder; the surface layer of oil was extracted with ether. Solvent was distilled off, and the residue was dissolved in water and converted into the picrate. Recrystallization from alcohol gave 1.65 g (73%) of picrate, m.p. 233°, undepressed by admixture of pure N-methylanabasine dipicrate.

N-Methylanabsine N'-Oxide. A solution of 2.6 g of N-methylanabasine N,N'-dioxide in 50 ml of absolute alcohol was cooled and saturated with a stream of dry sulfur dioxide. The solution was left overnight. After the removal of excess of sulfur dioxide by the passage of air and removal of alcohol under reduced pressure, a pale-yellow viscous substance was obtained. After treatment of this with saturated potassium carbonate solution, extraction with isobutyl alcohol, and vacuum distillation of solvent we obtained 1.85 g (77%) of base in the form of a viscous,hygroscopic yellow oil, which we did not succeed in crystallizing; pH > 8. For analysis the sample was vacuum-dried at 100°.

Found %: C 68.14; 68.22; H 8.14; 8.34; N 14.50; 14.42 $C_{11}H_{16}N_2O$. Calculated %: C 68.72; H 8.39; N 14.57

The dipicrate of N-methylanabasine N'-oxide was prepared in the form of yellow needles, m.p. 168.5-169.5° (from water or alcohol).

Found %: N 16.99; 16.93 $C_{23}H_{22}N_8O_5$. Calculated %: N 17.23.

The dihydrochloride of N-methylanabasine N'-oxide was prepared in the form of very hygroscopic colorless crystals; after being dried in a vacuum desiccator they melted at 179-181°; pH = about 4.5.

Found %: C 49.61; 49.81; H 6.69; 6.69 $C_{11}H_{18}N_2OCl_2$. Calculated %: C 49.82; H 6.84.

The reduction of N-methylanabasine N'-oxide was carried out under the conditons described above. From 0.05 g of base we obtained 0.09 g (54.6%) of picrate, m.p. 228.5-229.5°. A mixture with a sample of N-methyl anabasine dipicrate (m.p. 233°) melted at 228.5- 229.5°.

N-Methylanabasine N-oxide [4]. A mixture of 10 g of N-methylanabasine and 300 ml of 2.7% hydrogen peroxide solution was prepared and kept at room temperature for 40 days. Unchanged hydrogen peroxide was decomposed with platinum black. From 100 ml (one-third) of the solution (A) we isolated the picrate; from the remainder, after the usual treatment, we obtained 7 g (96%) of slightly colored, solid, very hygroscopic N-methylanabasine N-oxide base. For analysis the base was precipitated from benzene with heptane. The product consisted of colorless,hygroscopic crystals, m.p. 180-181°; pH = about 6.5. The crystalline N-oxide was vacuum-dried at 110°.

Found %: C 68.90; 68.95; H 8.40; 8.42; N 14.85; 14.82 $C_{11}H_{16}N_2O$. Calculated %: C 68.72; H 8.39; N 14.57.

The same N-oxide base was formed when N-methylanabasine was heated with 28.8% hydrogen peroxide in a boiling water bath for one hour. The picrate obtained from the reaction product was found to be identical with N-methylanabasine N-oxide dipicrate.

The dipicrate of N-methylanabasine N-oxide was prepared by addition of an aqueous solution of 8.25 g of picric acid to 100 ml of the solution (A). Crystallization of the precipitate from water gave 9.6 g (86%) of N-methylanabasine N-oxide dipicrate in the form of pale-yellow needles, m.p. 179-181°.

Found %: C 42.58; 42.66; H 3.27; 3.21; N 17.57; 17.34 $C_{23}H_{22}N_8O_{15}$. Calculated %: C 42.46; H 3.41; N 17.23.

The dihydrochloride of N-methylanabasine was prepared from the picrate by treating it with 1:1 hydrochloric acid. After being vacuum-dried at 110° the dihydrochloride melted at 175.5° (very hygroscopic); pH = about 4.5.

Found %: C 49.60; 49.80; H 6.81; 6.80; Cl 26.87; 26.57 $C_{11}H_{18}N_2OCl_2$. Calculated %: C 49.82; H 6.84; Cl 26.74.

Reduction of N-Methylanabasine N-Oxide. Reduction of 0.21 g of N-methylanabasine N-oxide base with zinc and hydrochloric acid gave 0.54 g (78%) of the picrate, m.p. 228-229°. A mixture with the dipicrate of N-methylanabasine (m.p. 233°) melted at 231°.

SUMMARY

1. The previously undescribed N-methylanabasine N-oxides were prepared: the N,N'-dioxide, the N'-oxide, the N-oxide, and their picrates and hydrochlorides.

2. The structures of N-oxides of N-methylanabasine were proved by their reduction with zinc and hydrochloric acid into N-methylanabasine, identified in the form of the dipicrate.

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SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, AND NITROGEN

V. A. Klimova and G. F. Anisimova

After carbon and hydrogen, nitrogen is the element that must be determined most frequently in the analysis of organic compounds. There can be no doubt about the expediency of determining it simultaneously with carbon and hydrogen, but there is no rapid and reliable method of doing this. The method that we propose for the simultaneous determination of C, H, and N consists in the pyrolytic decomposition of the substance in a rapid stream of oxygen in an empty combustion tube. Carbon and hydrogen are then quantitatively oxidized to carbon dioxide and water [1], but the nitrogen is obtained partly in the form of oxides and partly as elementary nitrogen [2,3]. The water, nitrogen oxides, and carbon dioxide formed are absorbed, respectively, with anhydrone, a solution of potassium dichromate in sulfuric acid carried on silica gel, and ascarite, and are weighed [4, 5]. Elementary nitrogen in admixture with a large excess of oxygen passes over a copper preparation in which oxygen is absorbed, and nitrogen is then displaced by carbon dioxide into a nitrometer, in which it is collected over KOH solution and measured. The nitrogen content of the substance is made up of the amount obtained as oxides and the amount obtained as elementary nitrogen.
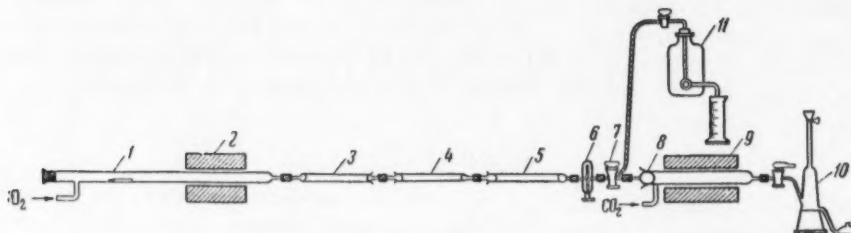
Apparatus for the simultaneous determination of C, H, and N: 1) combustion tube; 2) electric furnace; 3) 4) 5) absorption tubes for water, nitrogen oxides, and carbon dioxide; 6) terminal tube; 7) three-way tap; 8) tube containing copper preparation; 9) electric furnace; 10) nitrometer; 11) aspirator.

Pure oxygen is prepared by the catalytic decomposition of hydrogen peroxide in presence of cupric oxide. Oxygen is collected in a gas holder over saturated brine. For one combustion 500 ml is used. A control experiment with this amount of oxygen gives 0.032-0.037 ml of unabsorbed gas. The rate of passage of oxygen is 20-25 ml/minute.

For the preparation of the copper reagent, 300 ml of 40% NaOH solution was added to a solution of 150 g of $CuCl_2 \cdot 2H_2O$ in 1200 ml of water heated to 60°. To the reaction mixture we added 15 g of silica gel dried at 200° for 2.5 hours; the mixture was stirred and left overnight. The mass was then washed by decantation until it ceased to have an alkaline reaction (test with phenolphthalein); it was filtered. The dark-colored mass was dried with periodic stirring in a drying oven at 200° for 6-7 hours; it broke down into grains and was reduced in this form in a stream of hydrogen at 250-280°. The working temperature of the preparation was 250-280°; 1 g of it absorbed about 100 ml of oxygen.

TABLE

No.	Formula of substance	C (%) found	C (%) calculated	Δ	H (%) found	H (%) calculation	Δ	N (%) found	N (%) calculated	Δ
1	$C_7H_{15}ON_2$	53.36	53.50	0.14	9.39	9.55	0.16	26.81	26.75	0.06
		53.46		0.04	9.39		0.16	26.73		0.02
2	$C_6H_2(OH)(NO_2)_3$	31.42	31.44	0.02	1.25	1.31	0.06	18.25	18.34	0.09
		31.20		0.22	1.25		0.06	18.20		0.14
3	C_6H_5—C—C_6H_5 N—NH—$C_6H_2(NO_2)_3$	51.30	51.43	0.13	5.63	5.71	0.08	20.03	20.0	0.03
		51.60		0.17	5.67		0.04	19.83		0.17
4	$C_{12}H_{16}N$—NH—$C_6H_2(NO_2)_3$	61.41	61.29	0.12	6.53	6.45	0.08	15.2	15.05	0.15
		61.44		0.15	6.57		0.13	15.23		0.18
5	$C_3H_{15}ON_2$	59.51	59.67	0.16	8.25	8.29	0.04	23.38	23.20	0.18
		59.75		0.08	8.35		0.06	23.08		0.12

The apparatus is an arrangement for the rapid microdetermination of carbon and hydrogen [1] to the terminal tube of which a three-way tap has been attached; the tap is connected to a Mariotte vessel and to a glass tube filled with the copper preparation. The tube containing the copper preparation has a side tube connected to a Kipp apparatus, and the end, which is drawn out, is connected to the tap of the nitrometer (see figure).

For analysis a 2-8 mg sample of the substance to be analyzed is placed in a small beaker. The beaker is placed in the combustion tube, and 400-500 ml of oxygen is passed through the apparatus to remove air introduced with the beaker and as a result of diffusion into the absorption apparatus during weighing. The tube containing copper is now connected to the Kipp apparatus and checked for absence of air (presence of micro-bubbles in the nitrometer). The tap of the Kipp apparatus is then closed, the terminal tube is connected to the tube containing the copper preparation, and the combustion (pyrolysis [1]) is started. Combustion is continued for 20-25 minutes. When it is complete, the absorption tubes are weighed and nitrogen-containing substances are analyzed by the proposed method. The time required for analysis is 60-65 min. The results of the analyses are given in the Table .

SUMMARY

It was shown that carbon, hydrogen, and nitrogen can be determined simultaneously by the pyrolytic decomposition of the organic substance in a stream of oxygen in an empty combustion tube. Carbon and hydrogen are determined in the usual way, and nitrogen is determined from the sum of the amounts present as nitrogen oxides and as elementary nitrogen.

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Received February 14, 1958

LETTERS TO THE EDITOR

CALCULATION OF THE CONJUGATION ENERGY FOR THE
s-TRIPHENYLCYCLOPROPENYL CATION

In view of the announcement of the synthesis of the s-triphenylcyclopropenyl cation [1] we made a calculation for this compound by the LCAO MO method in the π-electron approximation. We started from the following assumptions: 1) the σ-skeleton is flat and has the C_{3v} symmetry group; 2) all the bond lengths are the same; 3) all the Coulomb integrals are equal to one another (and equal to α); 4) all the resonance integrals are equal to one another (and equal to β.); 5) the OA overlap integrals can be neglected.

The calculation showed the existence of a closed (in the Hückel sense) electron shell. In the system, 20 π-electrons occupy 10 molecular orbitals having energies (in order of increasing value) of: $\alpha + 2.61\beta$, $\alpha + 2.06\beta$ (doubly degenerate level), $\alpha + 1.79\beta$, $\alpha + 1.15\beta$ (doubly degenerate level), $\alpha + \beta$ (trebly degenerate level), and $\alpha + 0.76\beta$.

For this compound the conjugation energy is 9.16β, as compared with a system with isolated double bonds, and exceeds the sum of the conjugation energies in the phenyl rings and the cyclopropenyl cation by 1.16β.

<div align="right">D. A. Bochvar, I. V. Stenkevich, and A. L. Chistiakov</div>

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BEHAVIOR OF DIASTEREOISOMERS IN S_N2 REACTIONS

We have shown that the reaction of bromohydrins of type (I) with sodium phenyl sulfide RCHBr $-$CH(OH)R (I) + $C_6H_5SNa \longrightarrow$ RCH (SC_6H_5) $-$ CH(OH)R + NaBr proceeds in methanol by an S_N2 mechanism, and the threo- and erythro-isomers react at different rates. At 34° the ratios of the times of half-reaction of the erythro- and threo-forms are: 2 for 2-bromo-1,2-diphenylethanol ($R = C_6H_5$); 1.4 for 1,4-diacetoxy-3-bromo-2-butanol ($R = CH_3COO$); 1.2 for 3-bromo-2-butanol ($R = CH_3$). Hence, threo-isomers react more rapidly than erythro-isomers, and the difference in the reaction rates increases with the size of the substituent R. This phenomenon can be explained on the basis of conformation concepts if it is assumed that bromohydrins react in the conformation in which the smallest substituent on the asymmetric C atom adjacent to the reaction center (in this case hydrogen) is disposed in the same plane as the attacking agent [1]. In such a "reaction conformation " the substituents R are mutually transoid in the case of threo-bromohydrins and skew in the case of erythro-bromohydrins. For the erythro-isomers, therefore, a higher activation energy is required.

The dibromo compounds RCHBr $-$ CHBrR behave themselves in a corresponding fashion. Thus, of the two α, α'dibromobibenzyls, only the ($\pm$)-form gives α-bromo α' -(phenylthio)bibenzyl with C_6H_5SNa

(m.p. 61-65°; found %: C 65.03; H 4.58), whereas meso-α,α'-dibromobibenzyl is converted into trans-stilbene. In this case the different behavior of the diastereoisomers arises from the fact that the reaction conformation of the meso-form requires a skew orientation of the two phenyl groups, the steric repulsion between which is relatively great. Meso - and ($\pm$)-2,3-Dibromo-1,4-butanediols, in which the substituents R are smaller, react normally with C_6H_5SNa (though at different rates) with formation of stereoisomeric 2,3-bisphenylthio-1,4-butanediols, m.p. 77-79° (Found %: C 62.75; H 6.01; S 20.60) and 95-96° (found %: C 62.70; H 6.12; S 20.74). The results of conformation analysis indicated that the phenomenon of differing reactivities of threo- and erythro-forms in S_N2 reactions is general and should be detected also in other series.
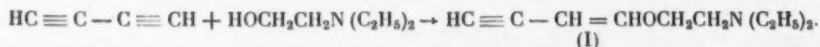
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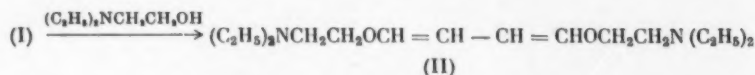of the Academy of Sciences of the USSR

The chemistry of butadiyne has recently attracted the attention of investigators. In this letter we report on some peculiar features of the reaction of butadiyne with some amino alcohols. It was shown that 2-diethylaminoethanol, unlike unsubstituted alkyl alcohols, reacts with butadiyne at room temperature in absence of catalyst with formation of 2-(1-buten-3-ynyloxy)-N,N-diethylethylamine (I) (yield 80-90%):

$$HC \equiv C - C \equiv CH + HOCH_2CH_2N(C_2H_5)_2 \rightarrow HC \equiv C - CH = CHOCH_2CH_2N(C_2H_5)_2.$$
(I)

2-Aminoethanol reacts with butadiyne under similar conditions, but with formation of the product of the addition of two molecules of amino alcohol to the butadiyne molecule (a compound related to the acetal of tetrolaldehyde), both at the hydroxy group and at the amino group (yield 70%).

The butenynyl ether (I) combines with a second molecule of 2-diethylaminoethanol under more vigorous conditions (at the boil under reduced pressure in presence of potassium ethoxide) with formation of 2,2'-(1,3-butadienylenedioxy)bis[N,N-diethylethylamine] (II) (yield 55-60%):

$$(I) \xrightarrow{(C_2H_5)_2NCH_2CH_2OH} (C_2H_5)_2NCH_2CH_2OCH = CH - CH = CHOCH_2CH_2N(C_2H_5)_2$$
(II)

The addition of butyl alcohol and ethanethiol to the butenynyl ether (I) also gives the corresponding 1,3-butadienes. In this the butenynyl ether (I) differs from alkyl butenynyl ethers, which undergo addition of the alcohol with formation of only tetrolaldehyde acetals. In the case of butyl alcohol, in addition to the diene we obtained the following acetal: $CH_3 - C \equiv C - CH(OC_4H_9)OCH_2CH_2N(C_2H_5)_2$. The structures of the products were proved by hydrolysis and spectrum analysis.

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METHOD OF SYNTHESIZING THE "A" RING OF TETRACYCLINES

In 1957 we described [1] the synthesis of tricyclic compounds in which two of the rings were similar in structure to the D and C rings of tetracyclines and the third, corresponding to the B ring, contained a double bond or a potential carbonyl group: this last fact created the prerequisites for the building up of the A ring of tetracyclines. We have now studied one of the methods of synthesizing this ring: the $CHX \cdot CO_2R$ grouping is introduced into the original ketone, the keto ester (I) is ethynylated, the acetylenic alcohol (II; $Y = C \equiv CH$) is hydrated in a neutral medium, and the hydroxy keto ester (II; Y = Ac) is cyclized into the dihydroxy ketone (III; Z = H), which is carbamoylated into the compound (III; Z = CONHR) by means of an isocyanate:

(I)   (II)   (III)
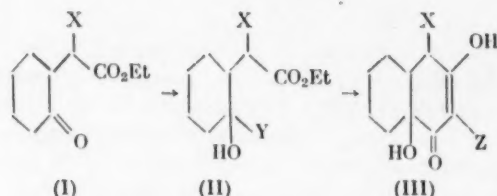
In a model synthesis the keto ester (I; X = H) was converted by treatment with $HC \equiv CNa$ in liquid ammonia ($-50°$, 1 hour) into the acetylenic alcohol (II; X = H, $Y = C \equiv CH$) (yield 85%, b.p. 84°/0.02 mm, $n^{17}D$ 1.4832. Found %: C 68.74; H 8.57). Similarly, the keto ester (I; $X = NMe_2$) (semicarbazone m.p. 176°; found %: C 55.21; H 8.52; N 20.00), obtained from cyclohexanone via oxocyclohexylideneacetic ester, was converted into the acetylenic alcohol (II; $X = NMe_2$; $Y = C \equiv CH$) (yield 60%, m.p. 97°; found %: C 66.47; H 9.10; N 5.68). The acetylenic alcohol ((II; X = H, $Y = C \equiv CH$) treated with $(AcO)_2Hg$ in EtOH (20°, 24 hours), was hydrated into the acetyl derivative (II; X = H, Y = Ac) (yield 65%, b.p. 92°/0.03 mm, $n^{17}D$ 1.4735. Found %: C 62.77; H 8.99), which was cyclized under the action of EtONa in EtOH (20°, 12 hours) into the dihydroxy ketone (III; X = Z = H) (yield 99%, m.p. 179°, λ_{max}^{EtOH} 263 mμ (log ϵ 4.14; $\underline{c}$ $2.4 \cdot 10^{-5}$), Found % C 65.97; H 8.10)*. The sodium enolate of this, treated with PhNCO (in $HCONMe_2$, 60°, 5 hours), gives the phenylcarbamoyl dihydroxy ketone (III; X = H, Z = CONHPh) (yield 40%, m.p. 151°, λ_{max}^{EtOH} 270 mμ (log ϵ 4.40, $\underline{c}$ $2.8 \cdot 10^{-5}$); found %: C 67.75; H 6.48; N 4.71).

M. M. Shemiakin, M. N. Kolosov, Iu. A. Arbuzov,
V. V. Onoprienko and G. A. Shatenshtein

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* This compound was synthesized simultaneously and independently by Huang Yao-Tseng and co-worker [2].
** Original Russian pagination. See C.B. Translation.

NIKITA ALEKSANDROVICH TOROPOV

(On the Occasion of his 50th Birthday)

Director of the Institute of Silicate Chemistry of the Academy of Sciences of the USSR, Fellow of the Academy of Building and Architecture of the USSR, eminent investigator in the silicate field, Professor Nikita Aleksandrovich Toropov was born on July 11, 1908. He graduated from the Geochemistry Department of Leningrad Polytechnical Institute in 1930. He was closely associated with Academician D. S. Beliankin as a student and investigator. Since graduating, he has been occupied in teaching work at the Lensoviet Technological Institute, Leningrad, first as lecturer, later as assistant professor, and since 1940, as professor. He organized a department of mineralogy in the insitute and arranged practical courses; he gave various courses of lectures (crystallography, mineralogy and petrography, crystal chemistry, physical chemistry of silicates). N. A. Toropov prepared more than twenty-five students for the degree of candidate of sciences who successfully defended their theses. Students of Toropov are to be found in various cities of the Soviet Union (L'vov, Chimkent, Sverdlovsk, Riga, Dnepropetrovsk, and others) working in various fields of technical petrography and physical chemistry of silicates.

Toropov's scientific investigations are of importance for the whole of the silicate industry and for other branches of technology. In the investigations carried out in his laboratories extensive use is made of improved crystal-optical methods and the ionization method of x-ray analysis; the synthesis of silicates at high temperatures, etc., is carried out.

It is characteristic of Toropov's scientific work that he knows how to formulate important fundamental tasks of a physicochemical nature on the basis of the material from investigations of technical products. Thus, work associated with the manufacture of alumina prompted the investigation of the systems $BaO - Al_2O_3$, $Na_2O \cdot Al_2O_3 - Na_2O \cdot Fe_2O_3$, and others. Having shown that in the reaction of nepheline with calcium carbonate, dicalcium silicate is formed as well as alumina and alkalis, he was able to define the basis of the complex treatment of nepheline.

N. A. Toropov developed many new methods of analytical and petrographic control which have received extensive application. The extension of petrographic methods in works owes much to Toropov's book on the petrographic control of cement clinker and slags. In view of the great importance acquired after World War II by nonmetallic magnetic materials (ferrites) in the technology of electrocommunications, Toropov is investigating various binary and ternary systems containing ferric oxide. For work on ferrites N. A. Toropov and a group of co-workers were awarded a Stalin prize.

A General Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR was held on February 27-28, 1958 under the chairmanship of Academicians A. P. Vinogradov and V. N. Kondrat'ev. Corr. Member Acad. Sci. USSR G. I. Chufarov read a paper on "Some Catalytic Phenomena in Processes for the Reduction of Metal Oxides and Sulfides". He pointed out that processes for the reduction of metal oxides and sulfides and other chemical compounds by solid and gaseous reducing agents are multistage in character; they include acts of adsorption of gaseous molecules of the reducing agent and desorption of gaseous reaction products, chemical reaction of the reducing agent on the surface of the oxide or sulfide, breakdown of the crystal lattice of the original substance and building up of the lattice of the solid reaction product, and diffusion in the solid phase. The breaking of old and formation of new bonds is here effected with direct participation of the reducing agent, which tears anions away from the crystal lattice by forming strong bonds with them.

In some cases the rate of removal of oxygen by the reducing agent is commensurate with the rate of diffusion of metal ions or oxygen in the crystal lattice. Hence, the over-all rate of the process is greatly affected by crystal-chemical transformations, and sometimes these form the slowest stage of the process, requiring the spatial redistribution of cations and anions. In these cases additions of substances that enhance the mobility of particles in the reaction zone should greatly accelerate the process, because they facilitate the surface migration of ions and so reduce the energy difficulties in the breakdown of one lattice and the building up of another.

The paper reported experimental material, obtained in the author's laboratory, on the accelerating effect of K_2O and Na_2O on the rate of reduction of oxides of iron, nickel, cobalt, copper, and manganese, zinc sulfide, nickel and cobalt ferrites, and other complex chemical compounds. In some cases the additives not only increase the rate of the process, but also change the type of kinetics of reduction. It was found that potassium and sodium compounds are specific in their accelerating effect.

G. I. Chufarov pointed out that investigations on the reduction of ferrites and of other more complex compounds are of special interest. In these cases the removal of oxygen by the reducing agent is accompanied by complex reconstruction of the lattice of the original substance into two new spatially distinct lattices. The difficulty of the crystal-chemical transformations in this case lies in the fact that macroscopic displacements must occur in ions that are uniformly distributed in the original substance. In such cases the effect of extraneous substances on the rate of reduction is particularly great. The experimental results on the effect of additives on the reduction of oxides, sulfides, ferrites, and other compounds find explanation on the basis of modern concepts of electronic processes occurring in semiconductors, such as the oxides and sulfides investigated, and determining their chemical properties. Potassium and sodium oxides, which were used as additives, have considerable volatility; as the author has shown, they are adsorbed on the surface of the oxide being reduced or on the reaction surface. As a result of electronic interaction of adsorbed potassium and sodium oxides with ions of the surface layer of the lattice, the mobility (migration) of ions is increased, thus facilitating the crystal-chemical transformations occurring during the reduction of metal oxides and sulfides. Moreover, the introduction of additives changes the concentration of electron and hole gas in these oxides and sulfides, which determines the reactivity of adsorbed molecules of reducing agent and therefore the rate of the process. The differences in electronic interaction between additives and the lattices of oxides and sulfides result in the position that the introduction of a given additive affects the reduction of different oxides differently, and a given oxide is reduced differently in presence of different additives. Numerous questions were addressed to the author.

L. A. Bliumenfel'd, Doctor of Chemical Sciences, read a paper on the "Migration of Electrons in Fermentative Catalysis, and the Structure of Proteins". At the beginning of his paper he mentioned the work carried out in 1954 by Commoner, Townsend, and Pake, who detected unpaired electrons in lyophilized vegetable and animal tissues by the method of electron paramagnetic resonance (EPR). Investigation of this phenomenon, study of the forms and breadths of EPR lines and of the conditions for their occurrence led the author to the conclusion that the unpaired electrons observed belong to the protein structures, but appear there only during the fermentative processes. These electrons arise from "impurity", and a substrate molecule that is temporarily forming a complex with the enzyme plays the part of a donor or acceptor "impurity". The form and breadth of the line indicates the great extent to which the unpaired electrons are delocalized in the protein structure. The

author suggested that this delocalization in native protein structures proceeds along regular chains of hydrogen-peptide bonds which pass across the main peptide chains and play the part of "conductivity channels".

In order to prove these hypotheses, L. A. Bliumenfel'd, in conjunction with A. E. Kalmanson, investigated the EPR spectra of free radicals appearing as a result of the γ-irradiation of amino acids, peptides, native and denatured proteins, and lyophilized tissues. It was shown that in the irradiation of dry preparations of amino acids and peptides there arise many positive ion-radicals having broad characteristic EPR lines, which usually have a hyperfine structure on account of the interaction between the magnetic moment of the unpaired electron and the magnetic moments of hydrogen atom nuclei. For native proteins the yield of radicals was only 10^{-3} — 10^{-4} as much, and the EPR lines were narrow and without hyperfine structure, similar to the EPR lines observed in fermentation preparations. These results showed that in native protein structures the electrons knocked out in the irradiation probably return to the "holes" along the "conductivity channels" The remaining "holes"with un-paired electrons are delocalized and give narrow EPR lines without hyperfine structure. Actually, as a result of preliminary heat denaturation, which destroys the regular network of hydrogen bonds, the irradiated proteins give broad EPR lines with a hyperfine structure, and the yield of radicals is increased 100-500 times. In the author's opinion, the concepts that he has developed enable us to make an approach to an explanation of some of the peculiarities of enzymic oxidation-reduction processes. V. G. Levich, Doctor of Chemical Sciences, and F. F. Vol'kenshtein, Doctor of Physical and Mathematical Sciences, took part in the discussion on this paper.

Corr. Member Acad. Sci. USSR D. N. Kursanov (co-authors M. E. Vol'pin and I. S. Akhrem) read a paper on "Investigations on the Aromatic System Tropylium". The author and his co-workers set themselves the task of investigating the tropylium ion as a new nonbenzenoid aromatic system which is also a stable carbonium ion. They therefore sought for new methods of preparing tropylium compounds and investigated the properties of these compounds. A study was made of the effects of various electrophilic reagents on cycloheptatriene, and it was found that many of these convert cycloheptatriene into tropylium salts. In some cases, e.g. under the action of phosphorus pentachloride, it was found that this reaction proceeds quantitatively.

Study of various tropylium salts enabled them to find some of very low solubility, suitable for the detec-tion of tropylium (e.g. the hexachloroplatinate, tetraphenylborate, and tetraiodomercurate). Tropylium tetra-phenylborate is interesting in that its anion is unable to form other than purely ionic links. This is a further confirmation of the nature of the C_7H_7 residue in tropylium salts. An investigation was made to determine with which ions tropylium forms ionic links and with which covalent links, passing in the latter case into cyclohepta-triene derivatives. Some matters relating to the reactivity of tropylium were studied; being a carbonium ion, it would be expected that tropylium would show some electrophilic reactivity. This view found experimental confirmation. It was found that tropylium salts are able to add at ethylenic bonds activated by electron-donat-ing groups, e.g. in vinyl ethers.

The author reported that tropylium salts react also with a great variety of organic substances containing active hydrogen (β-diketones, β-dicarboxylic acids, aldehydes, etc). It was found that benzene compounds having electron-donating substituents (phenols, naphthols) undergo analogous reactions. Dicyclohexatrienyl ether $(C_7H_7)_2O$ was found also to be capable of most of these reactions. These reactions, therefore, appear to provide a fairly general method of introducing the tropylium grouping into various organic substances. Acade-mician A. N. Frumkin, Corr. Member B. V. Nekrasov, Doctor of Chem. Sci. M. E. Diatkina, Candidate of Chem. Sci. G. V. Bykov, Doctor of Phys. Math. Sci. A. I. Kitaigorodskii, and others took part in the discussion.

G. A. Razuvaev, Doctor of Chemical Sciences, read a paper on "Reactions of Acyloxy Radicals in the Liquid Phase". He has carried out an investigation on the kinetics of the reactions of benzoyl peroxide and of acetyl benzoyl peroxide with alcohols, and these show that a chain process occurs: the radical formed by the removal of hydrogen from the alcohol initiates the breakdown of the peroxide. A study was made of the effects of various additions, liquids that mix with alcohols, 2,2-diphenyl-1-picrylhydrazyl, and metals,on the course of the reaction. According to their effects, liquid additives can be divided into the following groups: 1) those not affecting the reaction rate (water, acetic acid); 2) those having a limited retarding effect (benzene,cyclo-hexane, heptane); 3) those which retard the reaction greatly (trichlorobenzene, cumene); 4) those which react with the alcohol in presence of the peroxide (carbon tetrachloride). The addition of 2,2-diphenyl-1-pic-rylhydrazyl in very small amounts greatly retards the breakdown of peroxides in alcohols and has no effect on their breakdown in trichlorobenzene.

As the author pointed out, all these facts are readily explained by the proposed scheme for the process: primary breakdown of the peroxide into RCO_2 or R radicals, which remove hydrogen from the carbon atom attached to hydroxyl in the alcohol. The alcohol radical brings about initiated breakdown of the peroxide or, in the case of the addition of carbon tetrachloride, of the latter with removal of chlorine and formation of a new trichloromethyl radical. A chain reaction is thus initiated. In the decomposition of benzoyl peroxide labeled with C^{14} in the nucleus it was shown that transfer of the radical in the solvent proceeds in "relay fashion". According to their effects, metals added to alcoholic solutions of peroxides can be divided into the following groups: 1) metals that react with peroxide with the formation of salts (Zn); the alcohol does not take part in reaction; 2) metals which give one electron to the peroxide, which breaks down into an acyloxy anion and a radical which reacts further with the alcohol; 3) metals (Pt) which catalyze the reaction of the peroxide with alcohols. Mercury occupies a special position. In the cold it is converted into a mercurous salt by the peroxide When the reaction is carried out hot in benzene or acetic acid, organomercury compounds are formed. Investigation of the reaction mechanism showed that alkyl or aryl radicals, and also acyloxy radicals, in reacting with mercury salts of organic acids displace the acid radical, which, breaking down with liberation of CO_2, gives a new radical, which continues the chain reaction. As the author pointed out, the decarboxylation of mercury salts is brought about also by the action of light. Corr. Member of the Academy of Sciences of the USSR I. A. Kazarnovskii took part in the discussion on this paper.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

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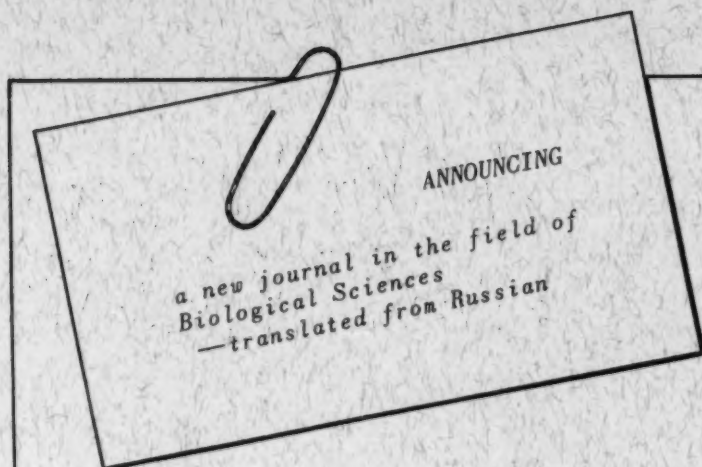
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Translated and published with the assistance of

the following companies in underwriting a

portion of the expenses involved:

Published Bimonthly
Starting with No. 1, 1959

ANNUAL SUBSCRIPTION: $25.00